

CHAPTER 4

SHEET FORMATION BY MELT BLENDING

4.1 Properties of Starting Material in Flat Sheet Form

Flat sheets of PBS and CAB (0.5-1.0 mm thickness) were prepared by melt-mixing and compression molding. PBS flat sheet is a flexible polymer, with a high EB of 94%, high tensile strength of 32 MPa and low %T of 0.19%. It has glass transitions temperature (T_g) at -31 °C, and a melting temperature at 111 °C.

For CAB flat sheet is high tensile strength of 34 MPa and low EB of 25%, which indicate that mechanically strong, tough and hard without being brittle. This polymer sheet is transparent with a high %T of 78%. The glass transition temperature of CAB was 107 °C and no melting temperature.

4.2 Binary and Ternary Blend Preparation by Melt-Mixing

Blend of PBS, CAB and plasticizer (Paraplex G40) in compound resin (0.5-1.0 mm) were prepared by melt-mixing technique from internal batch mixer. The compound was composed into flat sheet about 0.5-1.0 mm thickness by a compression-molding machine (LP-S-20, LabTech Engineering). PBS/CAB ratios were calculated to give blend compositions with 10 % by weight of Paraplex G40 as detailed in Table 4.1

Table 4.1 PBS/CAB blends compositions with 10 % by weight of Paraplex G40 prepared by melt-mixing.

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

4.2.1 Melt Flow Index

Melt flow index (MFI) is a measure of the melt of a thermoplastic polymer. It is defined as the mass of polymer, in grams, flowing in ten minutes through a capillary of a specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. The melt flow index of PBS/CAB blends (Table 4.2) and add 10 wt% Paraplex G40 compounds (Table 4.3) as shown in Figures 4.1-4.2. The MFI values of PBS is higher than CAB, which 6.84 g/10 min at 145 °C and 4.92 g/10 min at 170 °C, respectively. Viscosity to be more difference then it not tests at all the same temperature. The MFI of PBS/CAB blends due to increase with increasing of PBS content. Decrease of viscosity when adding CAB increase. The difference could be attributed to the interfacial interaction between PBS and CAB could react with the hydroxyl group of CAB to form ester bonds between these components, thus increased the melt flow properties of the compounds. Moreover, the MFI values of compounds increased when adding Paraplex G40 at 10% by weight.

Table 4.2 Melt flow index of various PBS/CAB blends.

PBS/CAB Composition	Melt Flow Index (g/10min) at 170 °C
100/0	6.84 (145 °C)
70/30	11.18
50/50	8.59
30/70	7.08
0/100	4.92

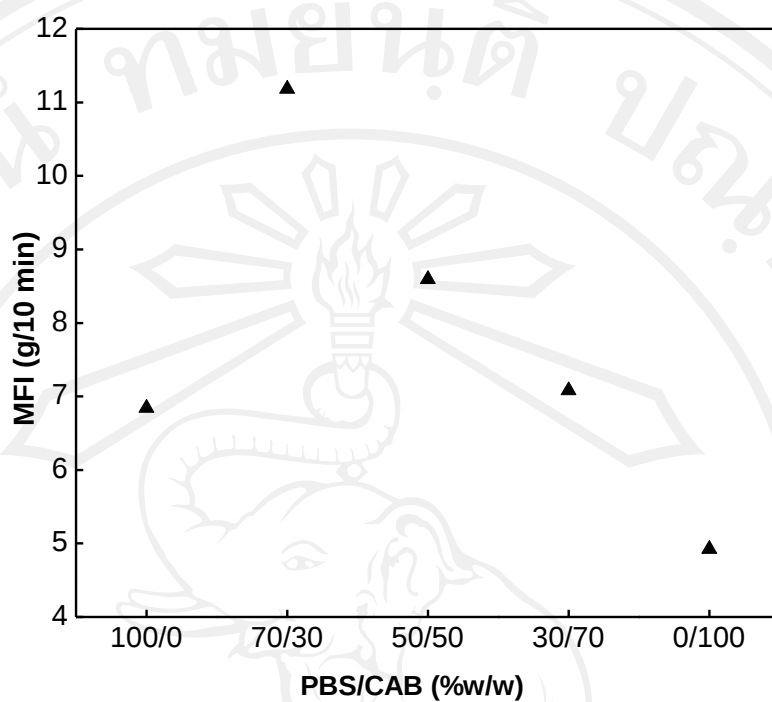


Figure 4.1 Melt flow index of various PBS/CAB blends.

Table 4.3 Melt flow index of various PBS/CAB blends with 10% Paraplex G40.

PBS/CAB/Paraplex G40 Composition	Melt Flow Index (g/10min) at 145 °C
100/0/10	9.35
90/10/10	11.59
80/20/10	11.15
70/30/10	10.72
60/40/10	10.08
50/50/10	6.44
40/60/10	3.12
30/70/10	2.39
20/80/10	0.41
10/90/10	0.29
0/100/10	5.92 (170 °C)

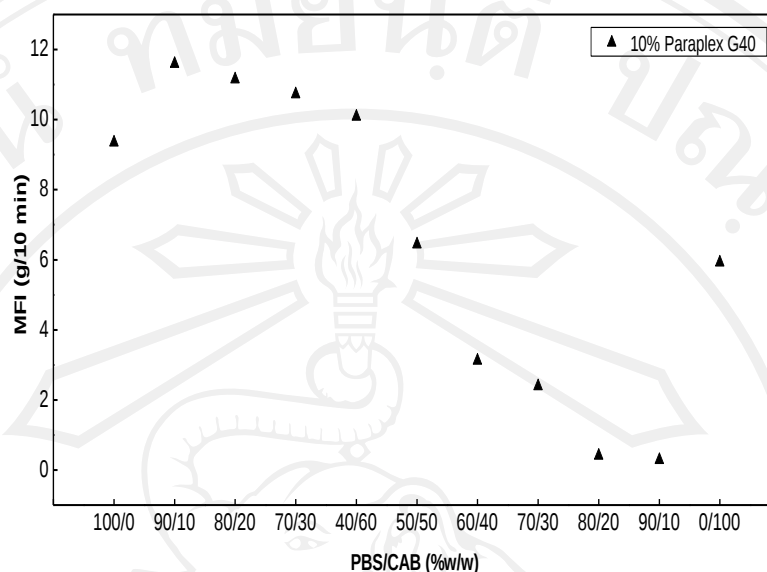


Figure 4.2 Melt flow index of various PBS/CAB.

4.2.2 Mechanical Properties

The tensile strength and elongation at break of the PBS/CAB blends were measured using tensile tests. The tensile test based on ASTM D 638 was carried out using a universal material testing machine with the dumbbell-shaped specimens at room temperature. The gage length was 65 mm, and the tensile test speed rate was 50 mm/min. Tensile strength, elongation at break and Young's modulus of polymer sheets of PBS, CAB and various PBS/CAB blends are shown in Table 4.4. PBS is high %EB (94%), and tensile strength (25 MPa) and flexible material. For CAB, it is high modulus (1,463 MPa), and tensile strength (34 MPa) and mechanically strong, tough and hard without being brittle.

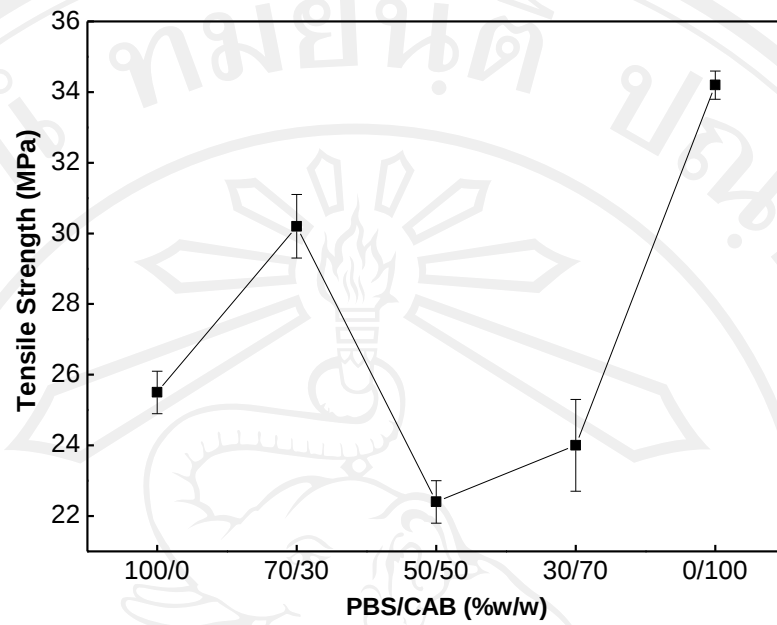
Figure 4.3 (a) show tensile strength of various PBS/CAB compositions. It is clear from this figure that high tensile strength of CAB. When adding PBS to cause decreased the tensile strength but not decreased all of blend composition. The tensile is increased again at composition of the PBS/CAB = 70/30. Result of percentage elongation at break is shown in Figure 4.3 (b). The percentage elongation at break (%EB) of the blends increased when increased weight % of PBS until the composition

PBS/CAB= 70/30, the %EB drastically increased by more than 230%. The %EB to drop when composition of PBS/CAB = 100/0. It was found that the addition of small amount of CAB was effective for plasticizing of PBS. It was postulated that this plasticizing effect of CAB on PBS was derived from the change in the crystalline state of PBS as mentioned above. The different crystalline state formed by a small amount of CAB could disturb the original crystalline state by an intermolecular interaction. The drastic change in the mechanical properties addition of a small amount of CAB coincided with the thermal properties. Specimens for composition PBS/CAB= 70/30 broke after necking and stress increased with the strain above the yield stress. However, for all the blends and neat CAB no yielding (brittle fracture).

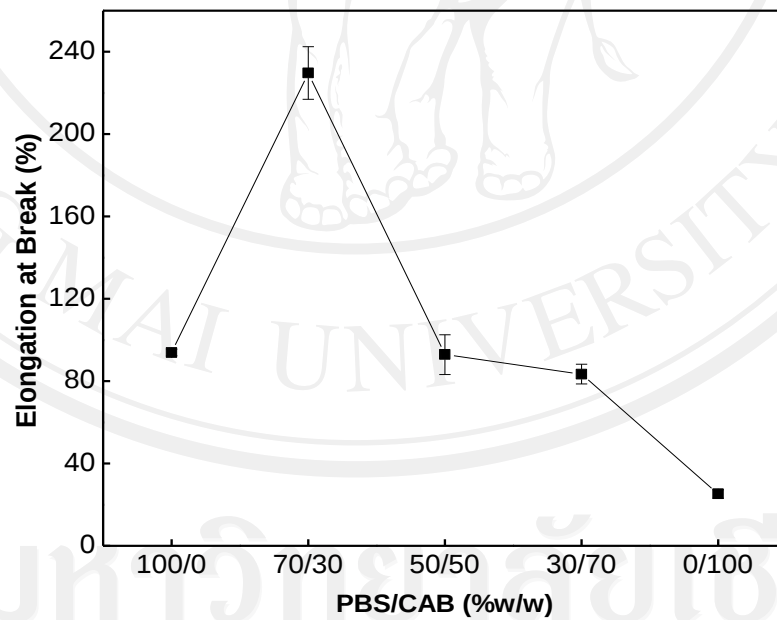
When plasticizer (Paraplex G40) was added to the PBS/CAB blend, The EB increased while both tensile strength and Young's modulus as compared without Paraplex G40 were observed over the whole composition range (Table 4.5 and Figures 4.4-4.5). The % EB of ternary blends was increase gradually with increasing PBS content. However, the high content of CAB, it was found that CAB was as an inhibitor for the biodegradation of polymer blends as mentions Therefore, ternary blends at 70/30/10 interested to development and improve for packaging application.

Table 4.4 Mechanical properties of PBS, CAB and various PBS/CAB blends.

Polymer Sheet	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
100/0	25.5±0.6	93.9±1.6	616.98±2.43
70/30	30.2±0.9	229.7±12.8	500.65±11.51
50/50	22.4±0.6	92.9±9.7	536.95±2.26
30/70	24.0±1.3	83.4±4.8	554.27±14.13
0/100	34.2±0.4	25.2±2.0	1462.99±21.70

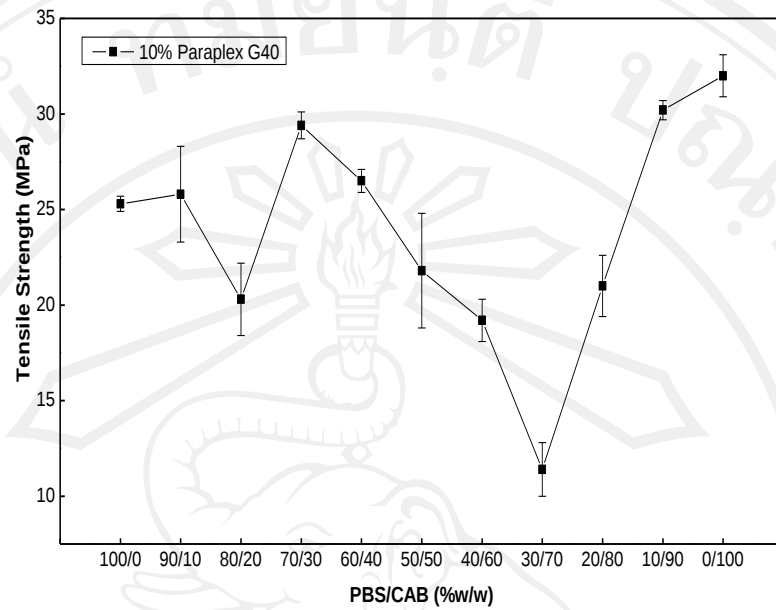


(a)

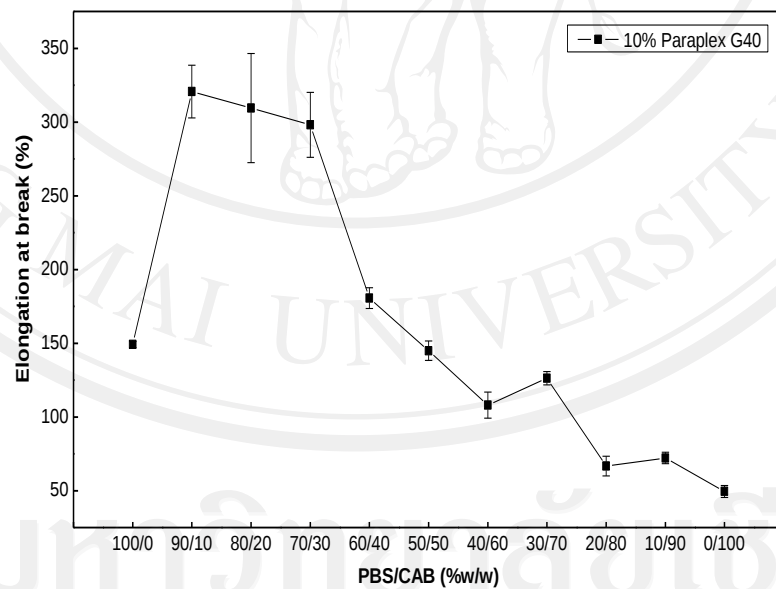


(b)

Figure 4.3 Mechanical properties of various PBS/CAB blends: (a) tensile strength and (b) elongation at break.

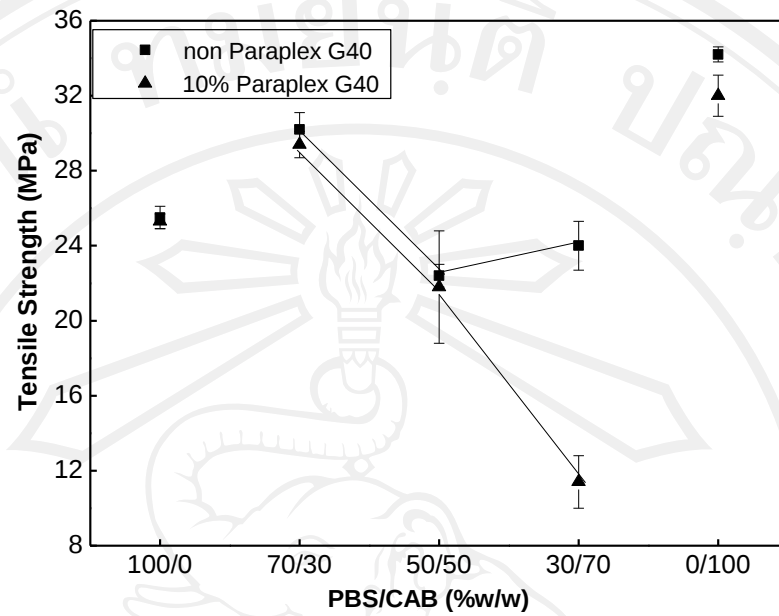


(a)

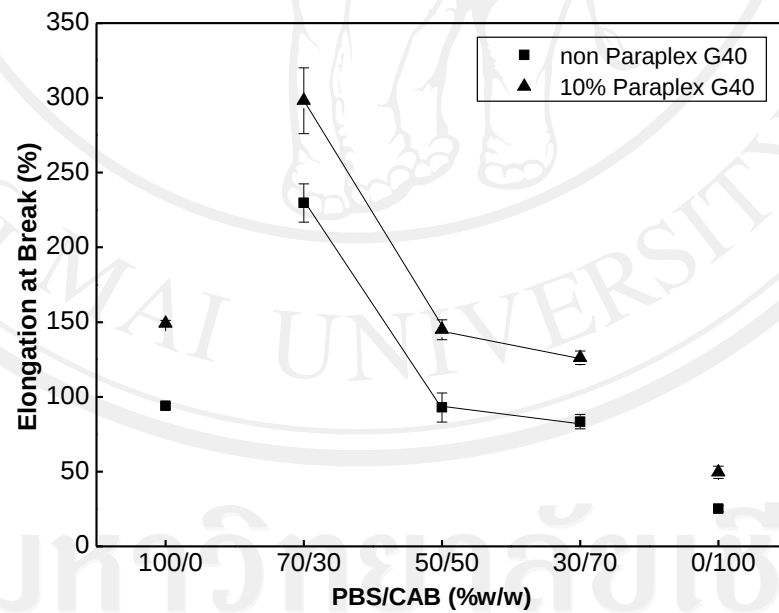


(b)

Figure 4.4 Mechanical properties of PBS/CAB blends without and with add 10 % by weight Paraplex G40 as a function of PBS/CAB compositions: (a) tensile strength and (b) elongation at break.



(a)



(b)

Figure 4.5 Mechanical properties PBS/CAB blends without and with add 10 % by weight of Paraplex G40 as a function of PBS/CAB compositions: (a) tensile strength and (b) elongation at break.

4.2.3 Thermal Properties

Thermal property characterization of the blends was performed with modulated DSC (Mettler 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 held 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.

Table 4.6 Thermal properties of PBS, CAB and various PBS/CAB blends with Paraplex G40 10% by weight.

PBS/CAB	Thermal properties			% Initial Crystallinity (%)
	T _g (°C)	T _c (°C)	T _m (°C)	
100/0	-30.9	97.5	110.8	45.2
70/30	-31.7	35.2	98.4	0.6
50/50	-16.6	n/d	n/d	n/d
30/70	23.9	n/d	n/d	n/d
0/100	107.1	n/d	n/d	n/d
100/0/10	-34.6	95.1	110.7	47.5
70/30/10	-32.5	25.6	100.4	17.0
50/50/10	-22.5	n/d	n/d	n/d
30/70/10	-3.2	n/d	n/d	n/d
0/100/10	94.0	n/d	n/d	n/d

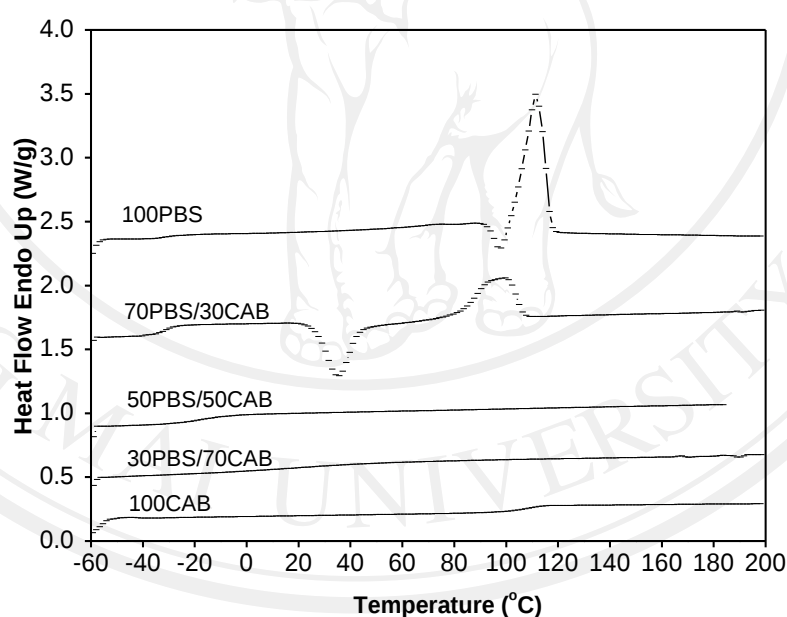
n/d = not detectable

ΔH_m° = melt enthalpy of 100% crystalline PBS (110.3 J/g)

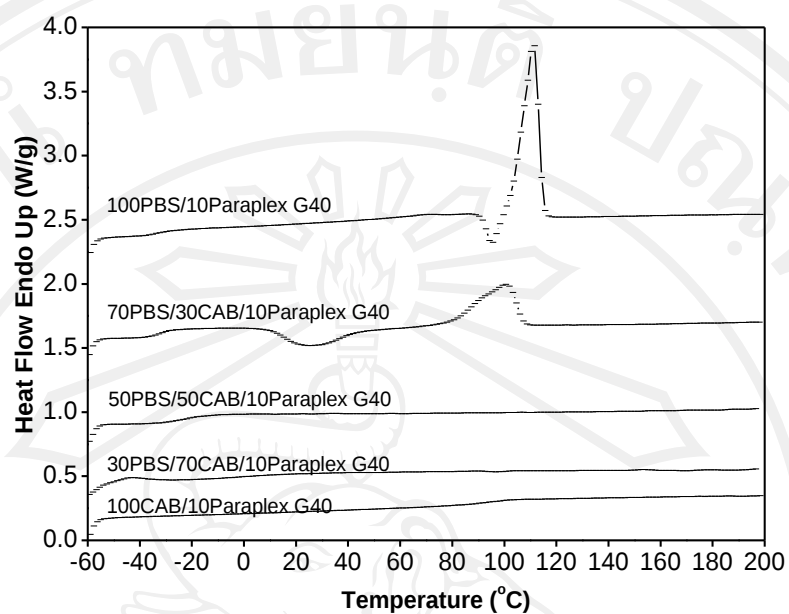
The results showed correspond to the second heating. Table 4.6 shows T_g and %initial crystallinity of PBS, CAB and PBS/CAB compounds. Figure 4.6 (a) shows the DSC thermograms of neat PBS, neat CAB and their blends. For neat CAB, a crystallization peak is not observed. For neat PBS, the thermogram shows a sharp melting peak at around 110°C. It also shows that the glass transition temperatures (T_g) of the neat PBS and the neat CAB is about -31 and 107°C, respectively. A direct

proof of polymer compatibility can be obtained by observing the change in T_g and T_m of both the polymers in the blend. A single T_g is observed for all blend compositions, which indicates that the polymer compounds is compatible. When increased weight% of CAB in PBS, T_g and T_m of PBS have changed, while as the composition of the CAB content increases the thermogram starts showing a endothermic peak shift towards lower temperature and continues for other blends.

Moreover, the addition of Paraplex G40 in PBS (see in Figure 4.6 (b)), it was found that Paraplex G40 considerably increased the %initial crystallinity of PBS. But, it not observed the crystallinity of neat CAB and up to 50 wt% of CAB (see in Figure 4.6 (b)). CAB molecule has a large and bulky group could be to interrupt the PBS chain rearrangement in polymer blends.



(a)



(b)

Figure 4.6 DSC thermograms of polymer compounds: (a) PBS/CAB and (b) PBS/CAB/10Paraplex G40.

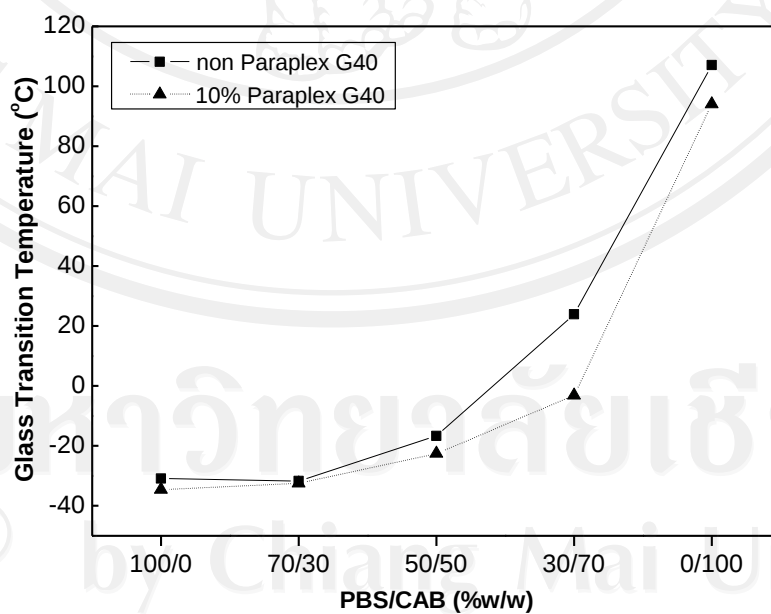


Figure 4.7 T_g of PBS/CAB blends with 10 % by weight Paraplex G40 as function of PBS/CAB composition.

The T_g decreases with the increase of weight% PBS because of a plasticization effect of the PBS molecules. Therefore, it seems that PBS molecule has a high compatibility with CAB molecule and PBS molecule is in an amorphous state. However, the T_g of the blend films is in disaccord with theoretical value of $T_{g \text{ CAB/PBS}}$ in the range from weigh% of PBS = 50 to weigh% of PBS = 70. These T_g show the nearly constant values located in approximately the same T_g of pure PBS. This result implies the presence of the pure amorphous region of PBS in the blend system. And the addition of Paraplex G40 in PBS/CAB blends reduced the T_g of PBS in the formations containing CAB (Figure4.7).

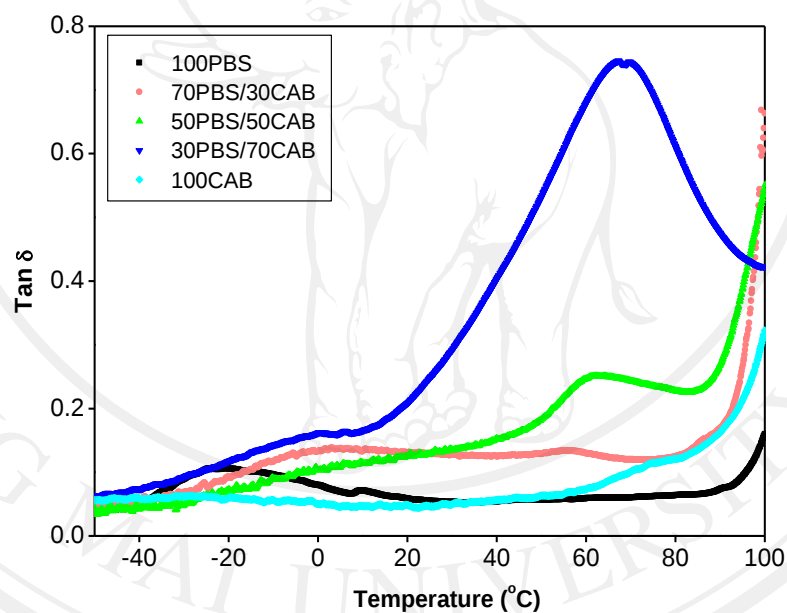
4.2.4 Dynamic Mechanical Properties

Traditionally, DSC is often used to determine the phase diagram of polymer blends, a single transition temperature indicating a single phase blend. However, DSC is not always sensitive enough to investigate the phase the phase behavior at the segmental level (limited to the determination of the domain size larger than 100 Å [Cowie, 1989]. The dynamic relaxation behavior of the PBS, CAB and PBS/CAB blends is presented by the temperature dependence of loss tangent ($\tan \delta$), storage modulus (E'), and loss modulus (E'') shown in Figure 4.8. Storage modulus is a measure of the energy stored and recovered in deformation whereas the loss modulus is a measure of the energy dissipated. $\tan \delta$ is the ratio of the energy lost to the energy stored in a deformation [Ren, *et al.*, 2009]. The sample were cooled to -50 °C and soon heated up to 110 °C at a heating rate of 4 °C/min under nitrogen atmosphere with frequency of 1 Hz. DMA not only provides information on mechanical characteristics and the temperature of phase transition, but also on the miscibility or compatibility of blends. The $\tan \delta$ indicates a loss of energy accompanying the motion of segment. Thus, the temperature of $\tan \delta$ (T_α) corresponds to T_g and is located in the T_g region. The DMA curve of pure PBS, CAB shows a marked drop in storage modulus (E') and a shape $\tan \delta$ peak around -30 and 100°C respectively, corresponding to glass transition. The storage modulus (E'), decreases as weight % of PBS decreases. And E' values of PBS is higher than that CAB, which is especially so in the rubbery state region.

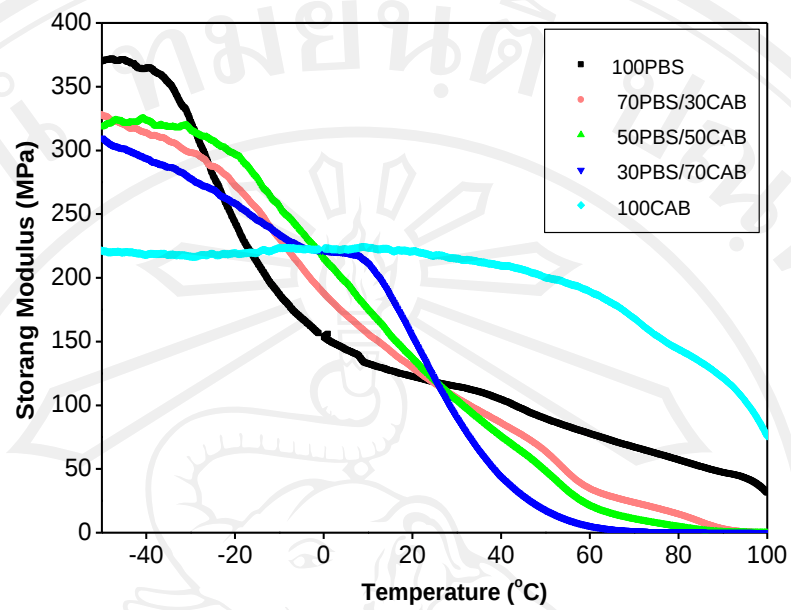
Table 4.7 Temperature of $\tan \delta$ (T_α) = T_g of PBS, CAB and various PBS/CAB blends.

PBS/CAB	Temperature of $\tan \delta$ (T_α) = T_g ($^{\circ}\text{C}$)
100/0	-20.5
70/30	1.7
50/50	62.4
30/70	69.7
0/100	n/d

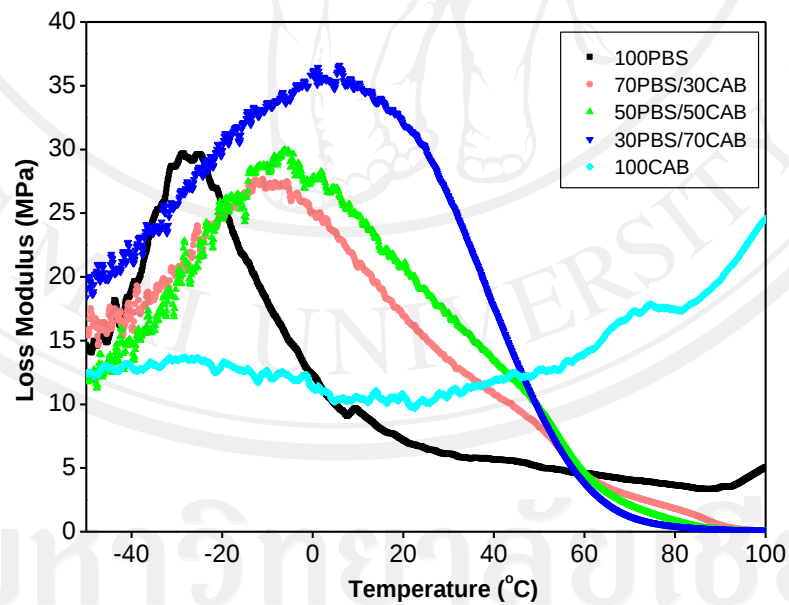
n/d = not detectable



(a)



(b)



(c)

Figure 4.8 Dynamic mechanical relaxation behavior composition of PBS/CAB blends sheets: (a) $\tan \delta$, (b) E' and (c) E'' .

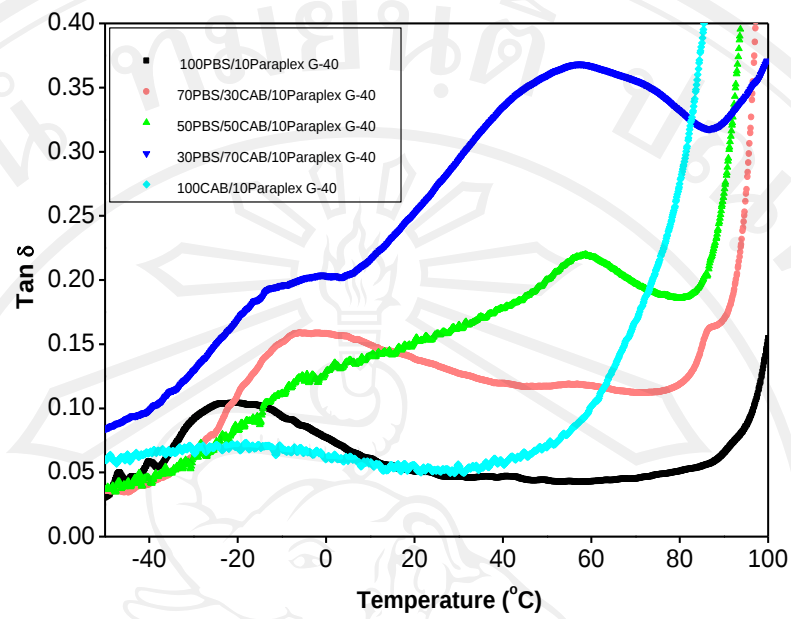
The loss tangent ($\tan \delta$ peak) indicates a loss of energy accompanying the motion of segment. Thus, the T_α corresponds to T_g and is located in the T_g region. Table 4.7 shows that the $\tan \delta$ values of PBS, CAB and various PBS/CAB blends. These $\tan \delta$ are clearly close to each other, which is consistent with the results of the above DSC analysis. DMA is useful for the determination of polymer blends compatibility because the T_α corresponds to T_g . Two independent T_g s generally indicate incompatibility of binary polymer mixtures. Figure 4.8(a) indicates that the PBS/CAB blends only exhibit one the T_α value between -20.5 and 69.7 °C. Accordingly, the PBS/CAB blends should be considered as compatible polymer blends. The T_α of CAB is higher than of PBS indicates that the characteristics of CAB were strong and hard. This result indicates that attack difficult of hydrolysis and enzymes, to cause a lower percentage biodegradation.

Table 4.8 Temperature of $\tan \delta$ (T_α) = T_g of various PBS/CAB blends with 10% Paraplex G40.

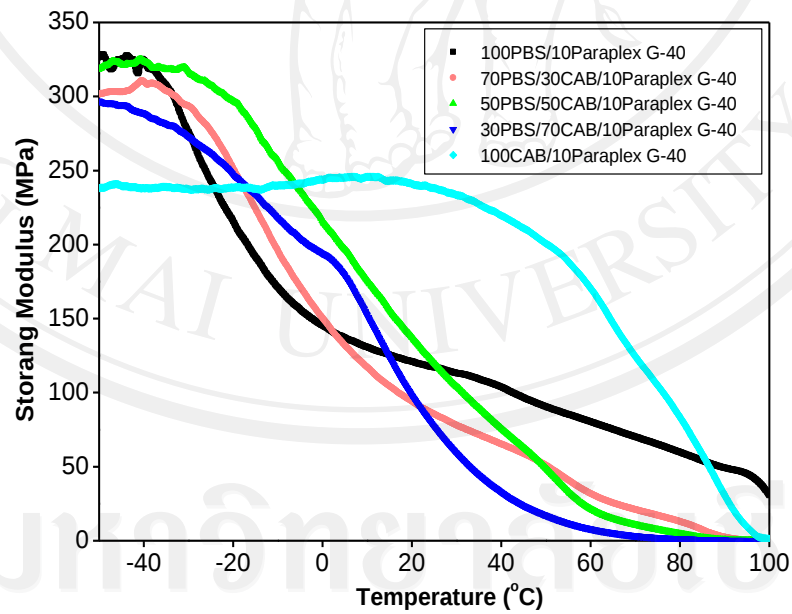
PBS/CAB	Temperature of $\tan \delta$ (T_α) = T_g (°C)
100/0/10	-20.8
70/30/10	-4.3
50/50/10	59.0
30/70/10	52.5
0/100/10	n/d

n/d = not detectable

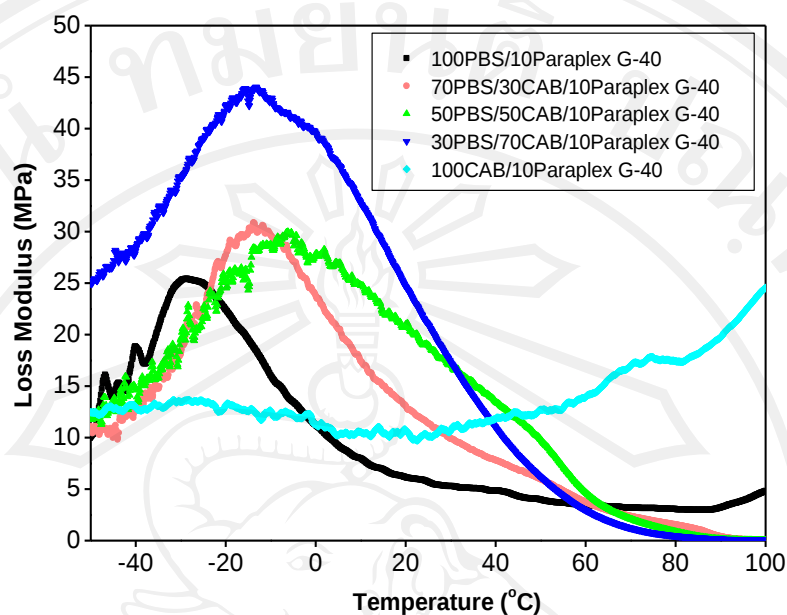
The efficiency of Paraplex G40 plasticizer in PBS, CAB and PBS/CAB was also appraised through DMA, its lead to reduced T_α (T_g) and show single T_α (T_g) indicating that the PBS/CAB blends should be considered as compatible polymer blends.



(a)



(b)



(c)

Figure 4.9 Dynamic mechanical relaxation behavior composition of PBS/CAB/Paraplex G40 blends sheets: (a) $\tan \delta$, (b) E' and (c) E'' .

4.2.5 Thermogravimetric Analysis

Thermal degradation of PBS, CAB and PBS/CAB blends was studied by determining their mass loss during heating. In figure 4.10 and 4.11 are presented the mass loss (TG%) and the derivative mass loss (DTG) curves at heating rate $50^\circ\text{C}/\text{min}$, temperature 50 to 600°C for PBS, CAB and PBS/CAB blends. From the thermogravimetric curves it can be seen that PBS and CAB present a relative good thermostability, weight remaining to be equal 0.9% for PBS and 8.3% for CAB. Range of degradation temperature (T_d) is $277\text{--}550^\circ\text{C}$ for PBS and $259\text{--}525^\circ\text{C}$ for CAB. In TG-thermograms one stage of mass loss can be followed, while in the DTG-diagrams, very small divergences from the peak regularity can be observed. These may be due to a second peak corresponding to small mass loss, taking place at the initial stages of thermal degradation, and thus it presents a particularly big covering (overlapping) with the peak that is corresponding to the main mass loss.

Table 4.9 Range of degradation temperature (T_d) of PBS, CAB and various PBS/CAB blends.

PBS/CAB	Range of Degradation Temperature (T_d)
100/0	277-550
70/30	279-525
50/50	285 -509
30/70	277-503
0/100	259-525

As it can see in the curves of DTG, in the early stages of the decomposition, there is a small shoulder probably due to a slight difference in the slope of decomposition curve of TG. And the DTG curves of PBS, CAB and various PBS/CAB blend indicates that single step decomposition.

Table 4.10 Range of degradation temperature (T_d) of various PBS/CAB blends with 10% Paraplex G40.

PBS/CAB/ParaplexG 40	Range of Degradation Temperature (T_d)
100/0/10	141 -492
70/30/10	234-524
50/50/10	287-511
30/70/10	181-523
0/100/10	287-511

The TGA traces and the first derivative (DTG) curves of PBS/CAB blends with 10 % by weight Paraplex G40 are shown in Figure 4.12 and 4.13. The DTG curves are chosen for the presentation because they more clearly show the difference in thermal stability between samples. It is clear from the figure that whatever the experimental condition, the PBS/CAB blends without Paraplex G40 each sample always shows higher overall thermal degradation temperature than that of the PBS/CAB blends with 10% by weight Paraplex G40.

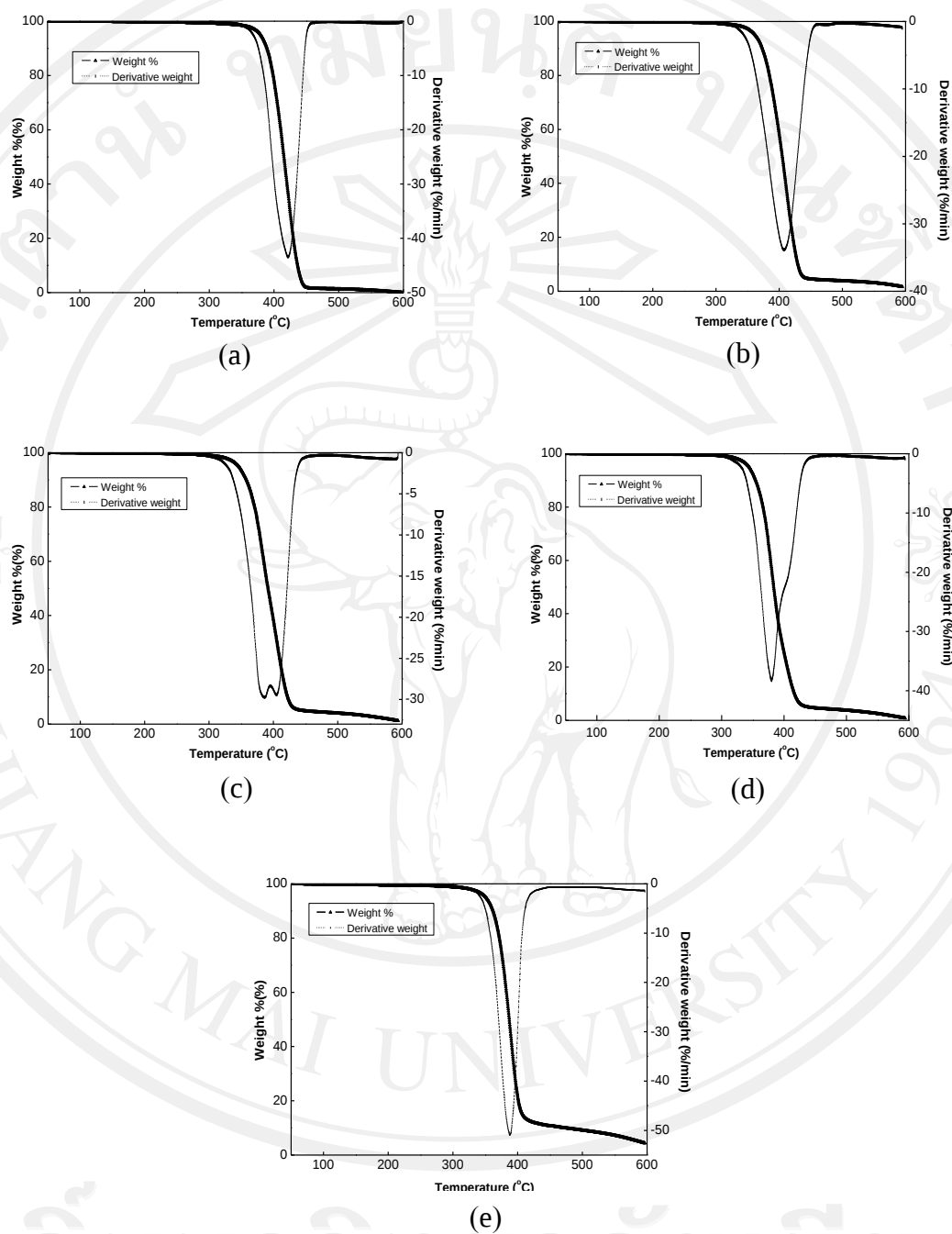


Figure 4.10 Mass loss (TG%) and derivative mass loss (DTG) vs temperature with heating rate 50°C/min : (a) 100/0, (b) 70/30, (c) 50/50, (d) 30/70 and (e) 0/100.

From the above result it is noticeable that PBS/CAB presents higher thermal stability than the PBS/CAB/Paraplex G40, it can be concluded that the number of methylene groups of used diol for Paraplex G40 preparation has a crucial effect on its thermal stability. As the number of methylene group increase, thermal stability decreases.

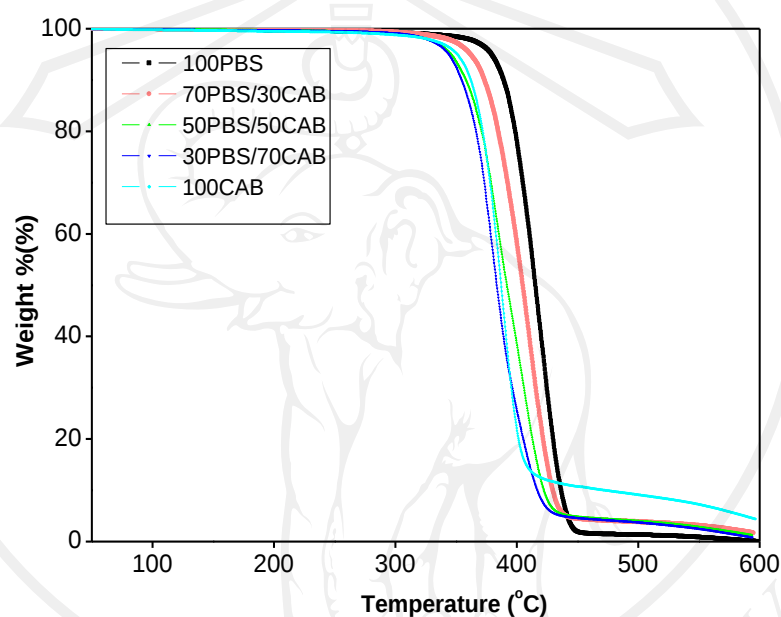
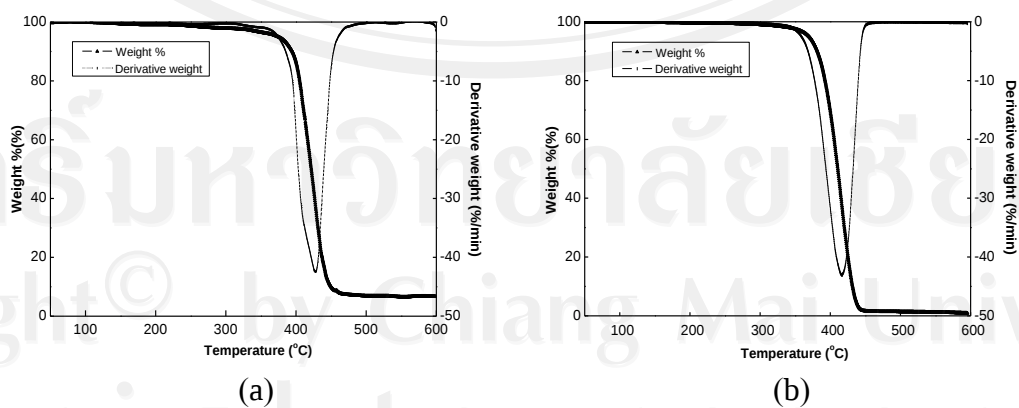


Figure 4.11 TG curves of PBS, CAB and various PBS/CAB blends.



(a)

(b)

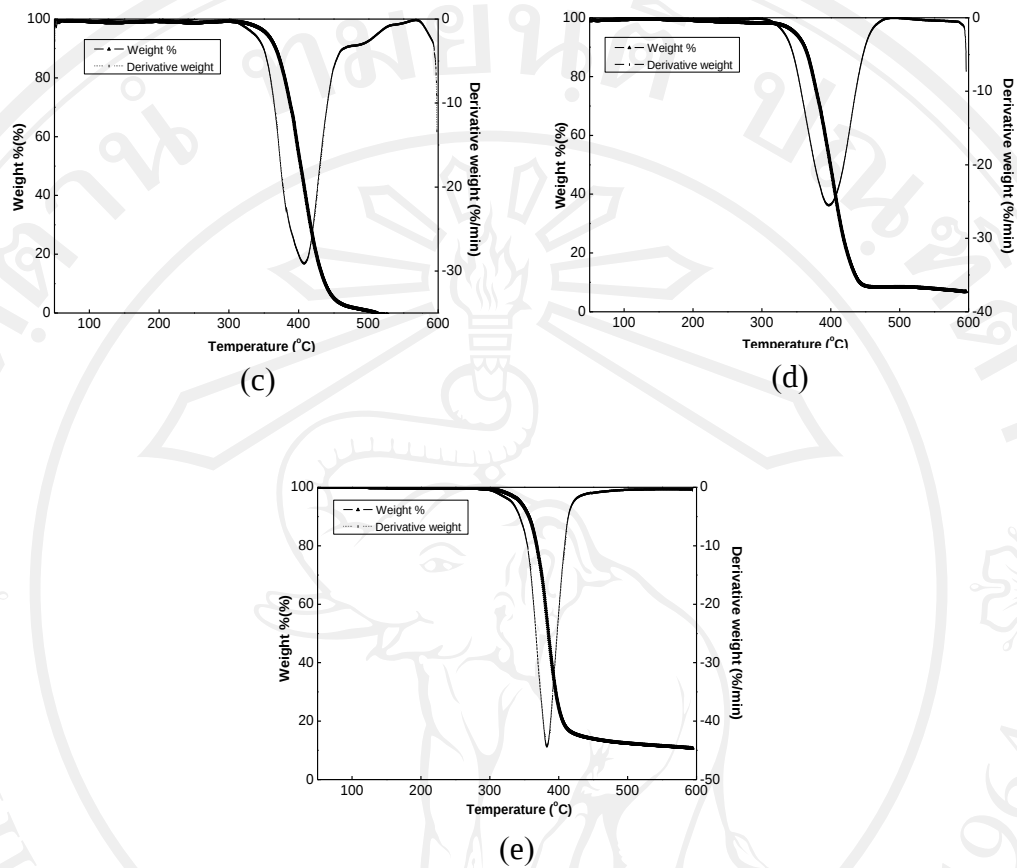


Figure 4.12 Mass loss (TG%) and derivative mass loss (DTG) vs temperature with heating rate 50°/min : (a) 100/0/10, (b) 70/30/10, (c) 50/50/10, (d) 30/70/10 and (e) 0/100/10.

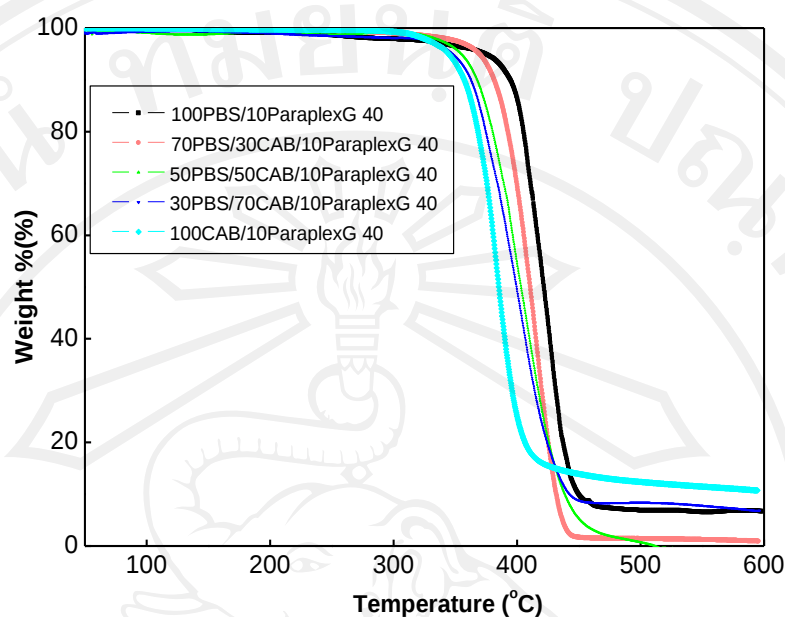


Figure 4.13 TG curves of PBS, CAB and various PBS/CAB blends with 10% Paraplex G40.

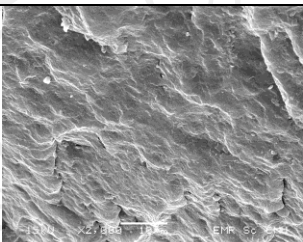
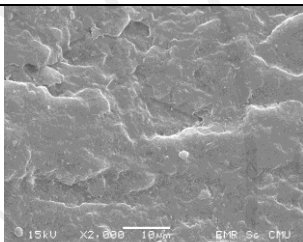
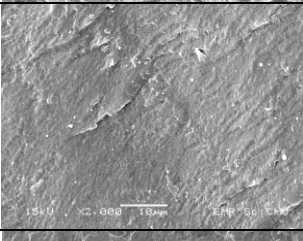
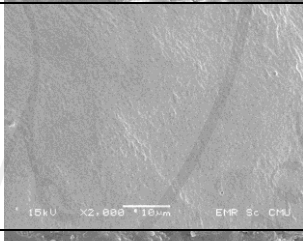
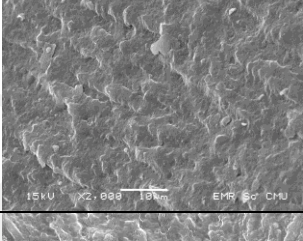
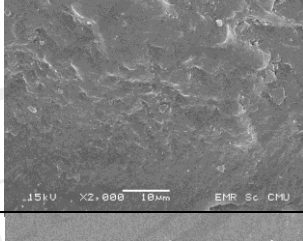
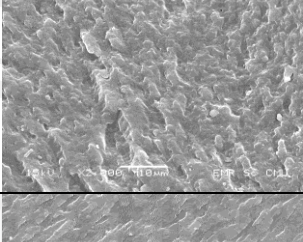
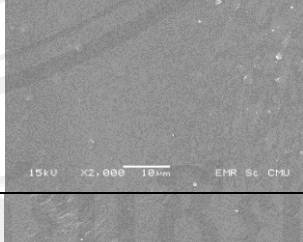
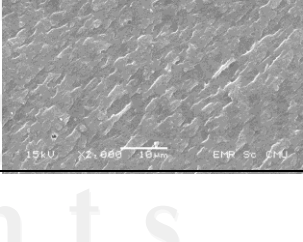
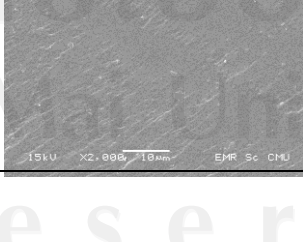
4.2.6 Morphology

The morphology of the polymer blend sheets was investigated with SEM and the polymer blends were fractured in liquid nitrogen. SEM images of fractured surfaces show the morphology of various blends of PBS/CAB without and with add 10% by weight Paraplex G40 are shown in Table 4.11.

From the fracture surface of neat PBS and PBS with add Paraplex G40 shows the phase, even though it has good compatibility, because it has an irregular fiber-shaped morphology, which results in a more extensive interface and low adhesion between the PBS and CAB. Paraplex G40 have relatively small mean diameter in PBS continuous matrix phase. SEM images of PBS/CAB show partial compatible morphologies without the cavity and rough resulting from poor interfacial adhesion but when add Paraplex G40 to cause increase surface smooth. For various PBS/CAB blend with Paraplex G40, PBS was clearly the continuous matrix phase with CAB and Paraplex G40 as filler in this three-phase system. The CAB and

Paraplex G40 particle are indeed small and a uniform distribution, indicating that partial compatibility between PBS, CAB and Paraplex G40.

Table 4.11 SEM images of various PBS/CAB blend with 10 % by weight Paraplex G40.

PBS/CAB (%w/w)	non-Paraplex G40	10% Paraplex G40
100/0		
70/30		
50/50		
30/70		
0/100		

4.2.7 Optical Properties

Table 4.12 and Figure 4.14 shows the result of the light transmittance test. The transparency of the blend films is around 30% up to weight% of PBS = 80. However, the transmittance (%T) decreases to estimate 17% at weight% of PBS = 50 and greater. The %T of PBS/CAB/Paraplex G40 blend sheets as shown in Table 4.10 and Figure 4.15. The %T value of PBS/CAB/Paraplex G40 blend sheets is around 0.2 to 75% and %T increased depend on amount of CAB in polymer blends. It indicates that the CAB to increase the transparency properties of polymer blends. The results of light transmittance test of PBS/CAB blends with 10% Paraplex G40 as plasticizer compared to PBS/CAB blends without plasticizer (Figure 4.16). The addition of Paraplex G40 slightly increased the %T of PBS/CAB system but slightly decreased at composition of PBS $\leq$ 50%. These finding suggest a partial compatibility of those polymers.

Table 4.12 Transmittance of various PBS/CAB blends with 10% Paraplex G40.

PBS/CAB (%w/w)	Transmittance (%)	
	non-Paraplex G40	10% Paraplex G40
100/0	0.19±0.05	0.21±0.05
90/10	-	0.28±0.04
80/20	-	0.85±0.52
70/30	1.33±0.11	2.59±1.25
60/40	-	8.24±0.94
50/50	17.67±2.03	17.55±1.35
40/60	-	19.09±4.07
30/70	70.18±2.84	27.02±4.61
20/80	-	75.47±1.55
10/90	-	75.93±1.12
0/100	77.53±0.21	77.86±0.66

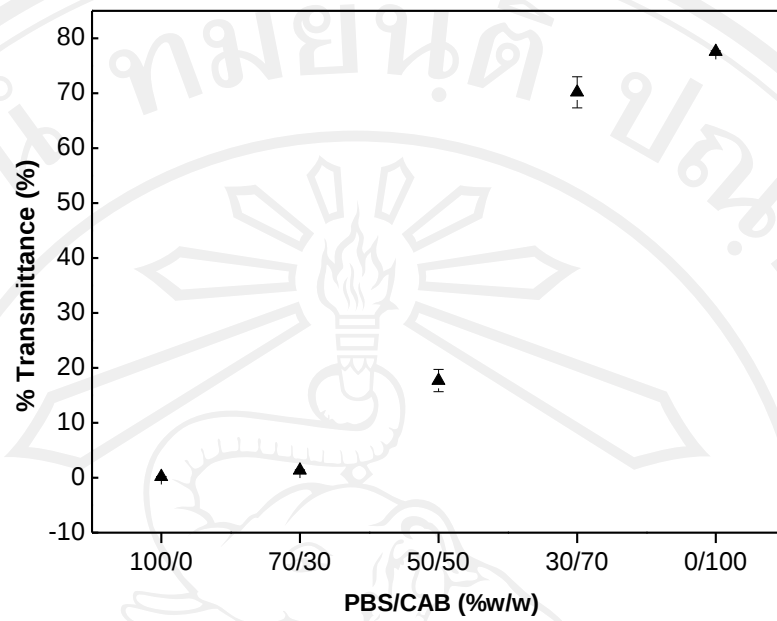


Figure 4.14 Transmittance of various PBS/CAB blends.

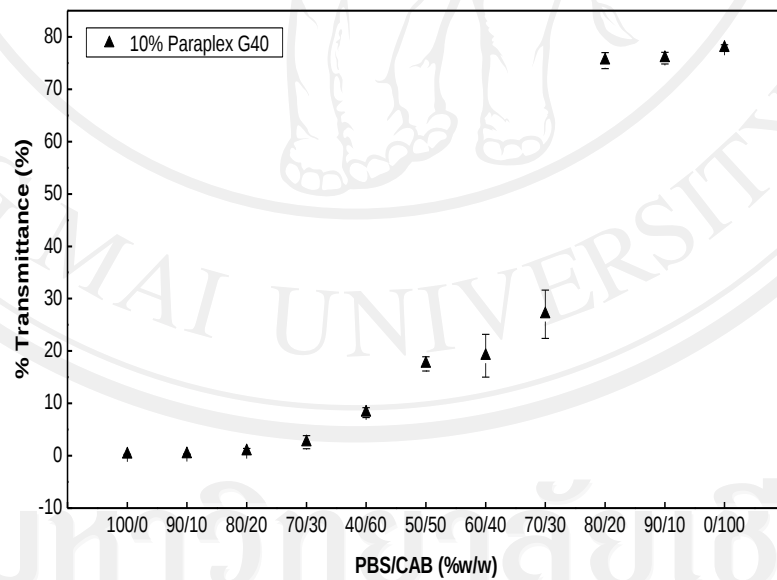


Figure 4.15 Transmittance of various PBS/CAB/Paraplex G40 blends.

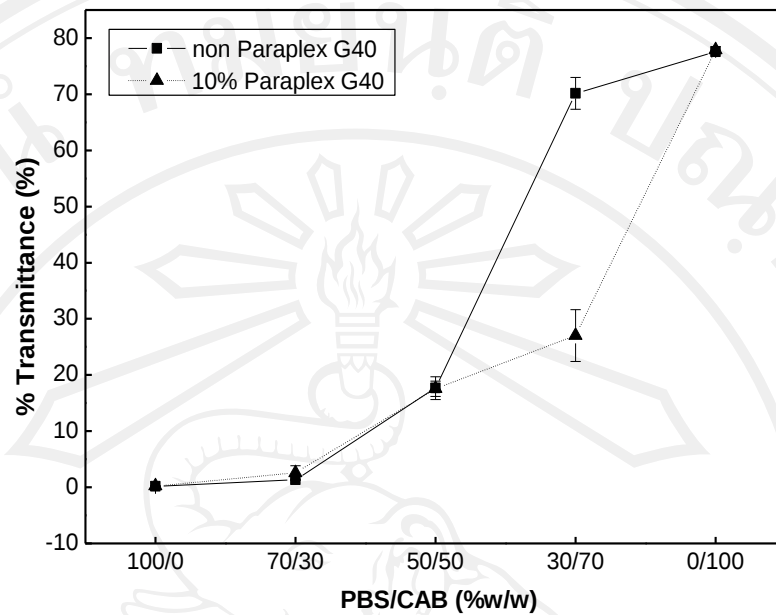


Figure 4.16 Transmittance of various PBS/CAB blends with 10 % by weight Paraplex G40 as a function of PBS/CAB compositions.

4.2.8 Biodegradation under Laboratory-Scale Composting Conditions

Determine volatile solid, organic carbon and carbon dioxide theoretical (ThCO_2) of all test substances are shown data in Table 4.13. The determination total carbon content of the test material by elemental analysis.

Determination of the theoretical quantity of carbon dioxide (ThCO_2) evaluation of polymer samples (include positive control and negative control) to be calculation as follow equation (1):

$$\text{ThCO}_2 = M_{\text{TOT}} \times C_{\text{TOT}} \times 44/12 \dots\dots\dots (1)$$

where M_{TOT} is the total dry solids in grams of test material, introduced into composting vessels at start of the test; C_{TOT} is the proportion of total organic carbon in the dry solids in the test material in grams.

Determination of the percentage biodegradability was calculated by comparing the amount of carbon dioxide in the sample (include positive control and negative control) with the blank by following equation (2):

$$\% \text{Biodegradation} = [(CO_2)_T - (CO_2)_B] \times 100 / ThCO_2 \dots\dots\dots (2)$$

where $(CO_2)_T$ is the cumulative amount of CO_2 evolved in each composting vessel containing the test material in grams; $(CO_2)_B$ is the cumulative amount of CO_2 evolved in blank (inoculums) vessel in grams; $ThCO_2$ is the theoretical carbon dioxide evolved, based on total carbon in sample. The composting test for PBS, CAB and PBS/CAB/Paraplex G40 blend sheets was carried out according to ISO 14855-1 in the controlled temperature at 58 °C. Figure 4.17 show the net cumulative CO_2 production of the cellulose (positive control reference), PBS, and PBS/CAB/Paraplex G40 (70/30/10) blend. PBS was found to degrade more than PBS/CAB/Paraplex G40. However, the amount of CO_2 produced for CAB was almost the same as that the inoculums.

Table 4.13 Evaluation volatile solid, organic carbon and carbon dioxide theoretical ($ThCO_2$) of all the test substances.

Sample	Dry weight (%)	Moisture (%)	Total dry solid (%)	Total carbon content (%)	$ThCO_2$ (CO_2 g/100 g sample)
Cellulose (Positive control)	95.24	4.76	100.00	43.52	159.57
LDPE (Negative control)	99.87	0.13	99.98	86.48	317.09
CAB	98.84	1.16	99.94	56.86	208.47
PBS	97.39	2.61	99.99	57.02	209.07
PBS/CAB/PG40 (70/30/10)	98.36	1.64	99.95	58.28	213.69

The resulting biodegradation profiles for cellulose, PBS, CAB and PBS/CAB/Paraplex G40 (70/30/10) blend can be seen in Figure 4.19 and the degree of degradation at 45 and 90 days are summarized in Table 4.14 (Standard of ISO 14855-1 and ASTM D5338, it must test biodegradation for time 180 days, but this project test biodegradation for 90 days because of face a problem flood at MTEC). The ISO 14855 test method is considered to be valid if the biodegradation degree of the reference material (cellulose) is greater than 70% after 45 days because it is made from natural resources; some of the three hydroxyl groups in glucose unit of cellulose are substituted for acetyl groups. At the end of 90 days, the results showed that the ultimate aerobic biodegradation under controlled composting conditions of LDPE, PBS and CAB were -0.72%, 79.67% and 1.92%, respectively. Under the same testing conditions, the biodegradation of cellulose, as positive control, was 91%. On the contrary for the LDPE film used as negative control sample no degradation signs were observed during in the compost. For PBS, is due to the fact that it first undergoes hydrolysis, which is a non-enzymatic reaction decreasing the molecular weight oligomers. After that the oligomers are consumed by microorganisms to evolve CO₂ after 7 day of the testing. Whereas, CAB powder did not undergo any biodegradation in the composting conditions within 90 days, due to the it has high T_g (~107 °C) and rigid polymer, which is difficult to hydrolyze in compost conditions. For PBS/CAB/Paraplex G40 (70/30/10) blends, the biodegradation value of 16% was obtained on the 90th day. When compare this with the PBS sample tested under same conditions, it can observe a lower percentage biodegradation more than PBS when adding CAB. Because of CAB were butyryl content 51%, acetyl content 4%, and hydroxyl content 1%, but CA is made from natural resources; some of the three hydroxyl groups in glucose unit of cellulose are substituted for acetyl groups. It is known that the biodegradability of CA depends on the degree of substitution (DS). Biodegradation can be observed in a sample with a DS of less than 2.5 [Sawada, & Fujimaki, 1994]. Since the hydroxyl groups in cellulose acetate are blocked and substituted by acetyl groups in various degrees, the biodegradability of cellulose acetate is less certain. The effects of the degree of substitution in each anhydroglucose unit on microbial attack have been intensively studied. These studies have shown that at least one substituent on every anhydroglucose unit resulted in

complete resistance to microbial attack on cellulose due to the chemical blocking of one or more of the hydroxyl groups. It was found that CAB additive was an inhibition for the biodegradation of PBS/CAB/Paraplex G40 blend. However, the PBS/CAB/Paraplex G40 blend ultimately biodegrade more slowly than required by ISO 14855-1.

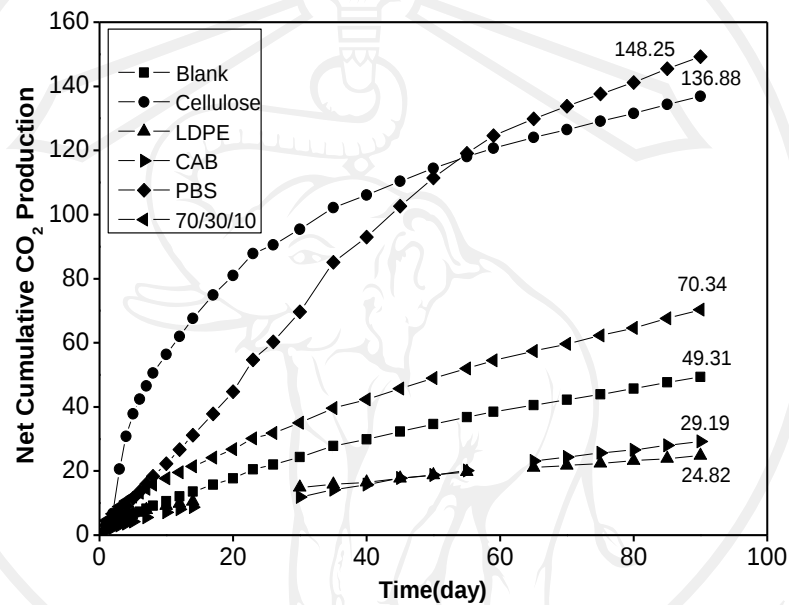


Figure 4.17 Net cumulative CO₂ production as a function of time for Blank(■), cellulose (●), LDPE (▲), CAB(▸), PBS(◆), 70/30/10 (◄).

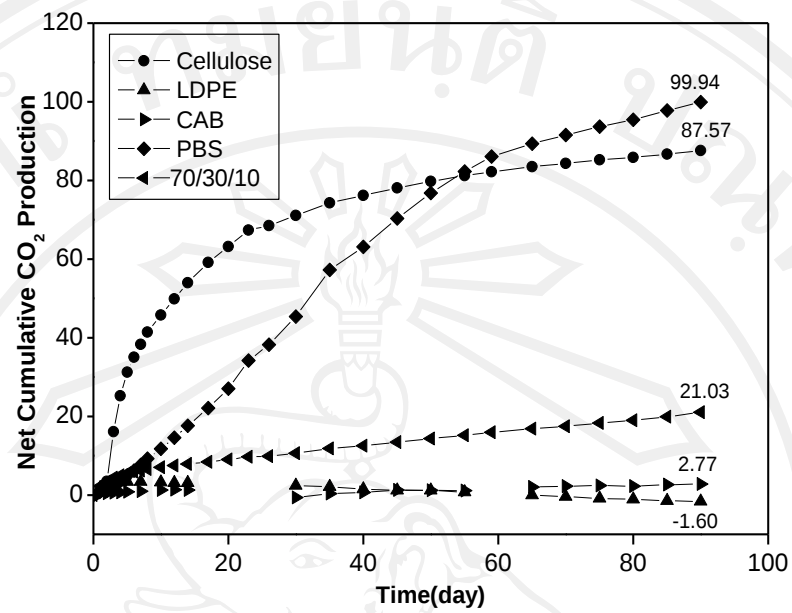


Figure 4.18 Net cumulative CO₂ production as a function of time for cellulose (●), LDPE (▲), CAB (▶), PBS (◆), 70/30/10 (◄).

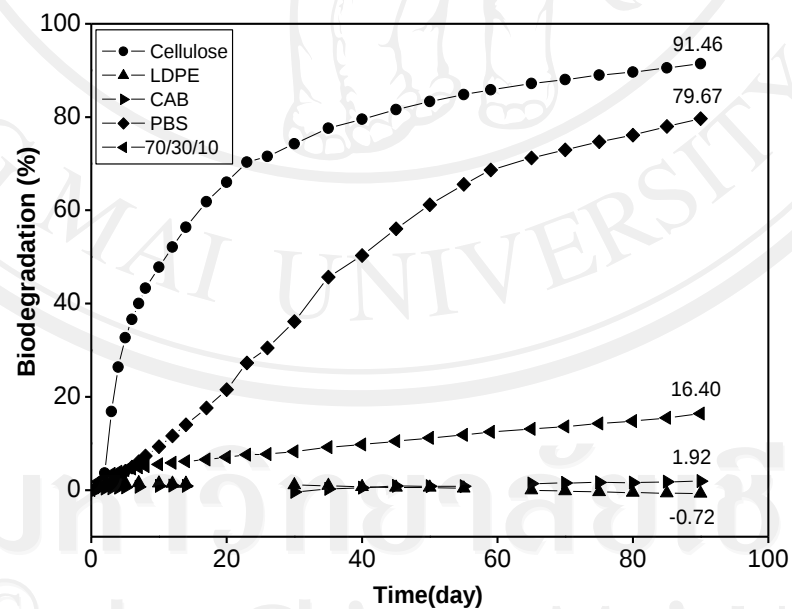


Figure 4.19 Degree of biodegradation as a function of time for cellulose (●), LDPE (▲), CAB (▶), PBS (◆), 70/30/10 (◄).

Table 4.14 Degree of biodegradation of cellulose, PBS, and PBS/CAB/Paraplex G40 blend as measured by the cumulative production of $^{14}\text{CO}_2$.

Sample	%Biodegradation (45 days)	%Biodegradation (90 days)
Cellulose (Positive control)	81.59	91.46
LDPE (Negative control)	0.54	-1.98
CAB	0.88	2.67
PBS	56.06	79.67
PBS/CAB/Paraplex G40 (70/30/10)	10.47	16.40