CHAPTER IV

RESULTS AND DISCUSSION

This study presents the poly (ethylene terephthalate) (PET)/ montmorillonite (MMT) nanocomposites prepared by solution technique. The mixed solvent of phenol 50 %v/v and tetrachloroethane 50 %v/v was used as a solvent. The PET solution concentrations were varied from 5 to 9 %w/v. The organoclay; montmorillonite modified with dimethyl dioctadecyl ammonium (2C18), was used to prepare PET/MMT nanocomposites which are comparing with the PET nanocomposite containing the unmodified ones. Two types of MMT were used at different clay content (1, 3, 5 phr) to produce nano-scale composites. The effects of PET solution concentration, MMT types (organoclay and neat MMT), and MMT content on the physical, mechanical, and thermal properties of the PET/MMT nanocomposites were investigated. The results from each characterization are demonstrated as following;

4.1   Physical Properties Characterization

4.1.1 Viscosity

The viscosity values of PET and its nanocomposite solution measured by Brookfield viscometer expressed in centipoises (cps) were listed in Table 4.1. The relationships of PET concentration with the clay content of both organoclay (2C18-MMT) and unmodified-MMT are graphically shown in Figure 4.1.

It can be seen that the viscosity of solution increases when increasing the concentration of PET. For example, considering at 3 phr organoclay contained nanocomposite solutions, the viscosity values of nanocomposite solution containing 5%, 7%, and 9% PET are 15.56, 19.00, and 26.25 cps, respectively. This trend is similar in evey formula as seen in Figure 4.1. That could be resulted from the increasing of number of chain entanglement when increasing the PET concentration. When the chain

entanglement increases, the shear force which is used to pass-through the solution system must be higher that is the cause of high viscosity value.

Table 4.1 Viscosity Value (centipoises) of PET and its nanocomposite solutions

Formula	Sample Code	PET (%w/v)	Unmodified-MMT (phr)	organoclay (phr)	Viscosity (centipoises)
1	5PET-0	5	-	-	15.56
2	5PET-A1		1	-	15.25
3	5PET-A3		3	-	15.00
4	5PET-A5		5	-	15.31
5	5PET-B1		-	1	14.50
6	5PET-B3		-	3	15.56
7	5PET-B5		-	5	15.69
8	7PET-0	7	-	-	20.50
9	7PET-A1		1	-	17.75
10	7PET-A3		3	-	17.88
11	7PET-A5		5	-	19.13
12	7PET-B1		-	1	18.44
13	7PET-B3		-	3	19.00
14	7PET-B5		-	5	22.00
15	9PET-0	9	-	-	25.50
16	9PET-A1		1	-	26.38
17	9PET-A3		3	-	25.50
18	9PET-A5		5	-	26.00
19	9PET-B1		-	1	25.25
20	9PET-B3		-	3	26.25
21	9PET-B5		-	5	27.13

Figure 4.2 shows the effect of clay type on viscosity value of PET/MMT nanocomposite solutions. It can be seen that the viscosity of both types of montmorillonite appears in the same trend upon increasing concentration. However, the viscosity of organoclay nanocomposite solution has a little higher compared to unmodified-MMT nanocomposite solution. It can be explained that the 2C18 modified MMT, which is more compatibility with PET than unmodified-MMT, can easily form

interaction force between polymer chain and silicate layer (clay layer), as a result organoclay nanocomposite solution needs more shear force to destroy or pass-through the solution system.

Considering the effect of clay content, it can be seen that the viscosity values of nanocomposite solution decreases when adding 1 phr of both types of clay. However, when increasing the clay content up to 3 phr the viscosity values of nanocomposite solutions start to increase, as seen in Figure 4.2. For instance, the viscosity values of 7 % PET solution containing 1, 3 and 5 phr unmodified-MMT are 17.75, 17.88 and 19.13 cps, respectively, while those of 7% PET solution containing 1, 3, and 5 phr organoclay are 18.44, 19.00 and 20.00 cps, respectively. This phenomenon can be explained that the added clay in the solution may interfere with the PET chain entanglement resulting in the lowering of shear force and viscosity value. Nevertheless, when further increasing the clay content, the viscosity tends to increase because of the interaction force that would be discussed as followed.

As know that the interaction between polymer chains are an important factor. The interaction between polymer chains should be decreased when adding clay into the polymer solution because of the intercalation of polymer chain and interspacing silicate layer and the swelling effect from the mixed solvent. However, the viscosity values tends to be increased when the system has a lot of clay containing because the chance of intercalation of polymer chains was reduced by the clay agglomeration and the increasing of the interaction of polymer-polymer chain, clay-polymer chain and clay-clay as well.
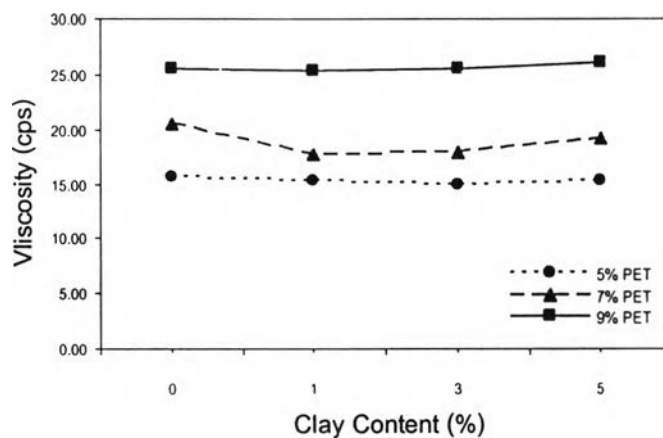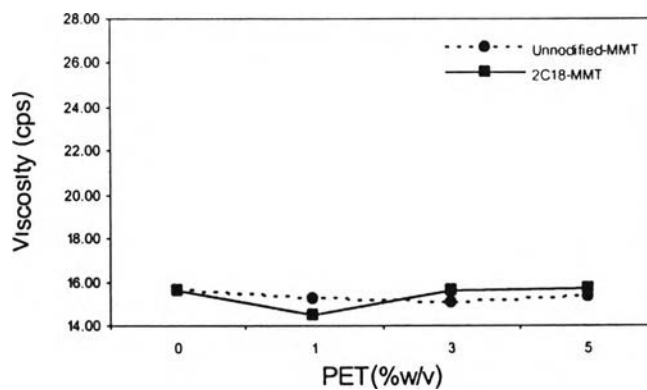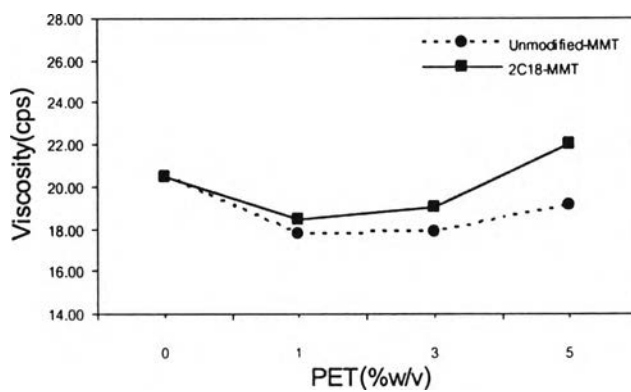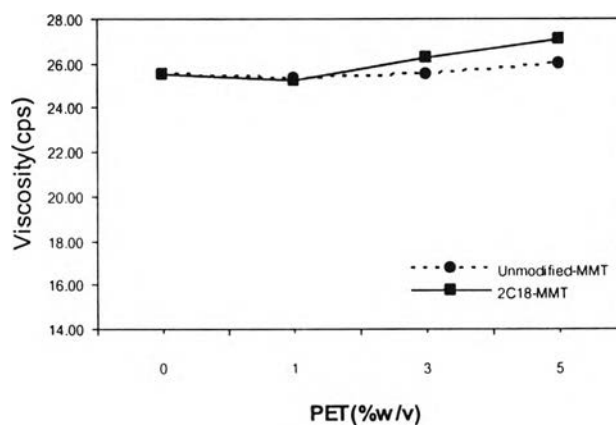
(a) unmodified-MMT
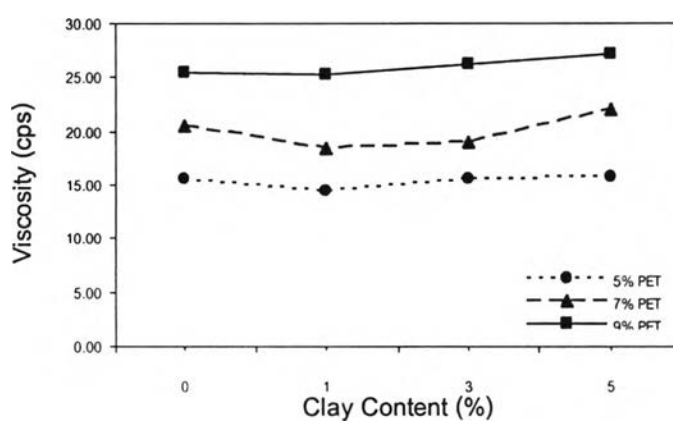
(b) organoclay

Figure 4.1 The relationship between viscosity and PET concentration of the nanocomposite solution containing 1, 3, and 5 phr (a) unmodified-MMT (b) organoclay

(a) 5 %PET

(b) 7 %PET

(c) 9 %PET

Figure 4.2 The effect of clay type on viscosity of the PET/MMT nanocomposite solution
at various PET concentration; (a) 5 %w/v, (b) 7 %w/v, and (c) 9 %w/v

4.1.2 Physical Structure

4.1.2.1 X-ray Diffraction (XRD)

The intercalation between clay and polymer matrix can be relatively demonstrated by the enlargement degree of interlamellar distances. The interlamellar distances can be calculated by the diffraction peak and its position of d_{001} by the x-ray method, the values of which are calculated by Bragg equation [22] shown below:

$$2d_{001} \sin \theta = n\lambda \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(4.1)$$

Where d_{001} is the inter planar distance of (001) diffraction face (Å)

θ is Bragg angle of the reflection (degree)

λ is the X-ray wavelength (Å)

n is an integer

The X-ray diffraction pattern for PET and its nanocomposites was obtained from an analysis of film sample. Figure 4.3 shows the x-ray diffractogram of clays: unmodified-MMT and organoclay, and its nanocomposite. From this figure, the measured d_{001}-spacing, which calculated from equation (4.1), of unmodified montmorillonite (unmodified-MMT) is 12.5 Å which occurs approximately at $2\theta = 7.0°$ and the d_{001}-spacing of dioctadecyl dimethyl ammonium modified montmorillonite (2C18-MMT) is 31.4 Å, 18.3 Å, and 12.3 Å which occurs approximately at $2\theta = 2.8°$, 4.1°, and 7.1°, respectively. The (001) plane peak of the organoclay is shift lowering to low angle compared to the unmodified-MMT. The higher degree of basal spacing expansion usually results from the effect of intercalation. In this case, dioctadecyl dimethyl ammonium in the cationic from underwant cationic exchange reaction with Na$^+$ and Ca$^+$ ions, producing organoclay of dioctadecyl dimethyl ammonium intercalated in montmorillonite. In other words, the intercalation occurred and the *d-spacing* of the clay increased by the organo-modification.

For the unmodified-MMT nanocomposite films, as shown in Figure 4.4, the nanocomposites containing 1 to 5 phr of unmodified-MMT show no peak of clay in

XRD pattern probably due to the fact that the added amount of clay is too low to detected, whereas, the XRD pattern of 10 phr unmodified-MMT contained nanocomposite shows clay peak at $2\theta = 5.5°$ which is corresponding to the d_{001}-spacing of 15.9 Å. Comparing with the clay peak of unmodified-MMT occurring at $2\theta = 7.0°$, the shift of a diffraction peak towards lower angle value [$2\theta = 7.0°$ (12.5 Å) to $2\theta = 5.5°$ (15.9 Å)] is likely due to the further expansion of layered silicate platelets occurring during the processing.   This result can be indicated that intercalation occurred because of the increasing of d-spacing by polymer chain intercalation related to the appeared clay peak shift to lower angle. It should be resulted from the method used to prepare the nanocomposite film which is the use of solution technique and power of ultrasonic energy.   Similar to the work done by G. Liang et al [10], they concluded that the blending process can affect on intercalation behavior. The results from XRD show the disappearance of the (001) plane peak of organo-MMT in nanocomposite prepared by solution blending compared with nanocomposites prepared by direct melt intercalation process.

Similar to the unmodified-MMT, generally, the intercalation of the polymer chains usually increases the *d-spacing* of clay in comparison with the spacing of the organoclay used, leading to a shift of the diffraction peak towards lower angle values. However, considering the XRD diffraction pattern of 2C18-MMT nanocomposite films, the nanocomposite containing 1 to 5 phr of 2C18-MMT showed no obvious clay peak around $2.0° - 7.0°$ in the XRD pattern as demonstrated in Figure 4.5. Moreover, with increasing the organoclay content up to 10 phr, the XRD pattern still shows the same as those of lower organoclay content (1-5 phr). It might be assumed that most silicate layers lose their crystallographic ordering in the nanocomposite and the exfoliation of organoclay occurs. Similar to the study of PETN/organoclay nanocomposite by J.H. Cheng et al (2001) [52], which indicated that the clay particle may be highly dispersed in the polymer matrix without a large agglomeration of its particle for low organoclay concentration (< 4 wt %). Also, it may be resulted from the much lower concentration of organoclay.   Therefore, in order to confirm this result the transmission electron microscopy (TEM) should be performed to identify the structure in nanoscale level

whether an exfoliated structure is really achieved in this case.

Moreover, WAXD is also used as a tool to study the crystallization behavior of polymer. Different studies have been carried out in order to determine the crystal structure of PET nanocomposite. As seen in Figure 4.4 and 4.5, the X-ray diffraction peak of PET and its nanocomposites films consist of a broad amorphous halo and peaks centered at $2\theta = 16.6°$, $22.5°$, and $25.4°$ that are associated with PET crystallites [28]. Upon increasing the clay content, the diffraction curves show a gradual increase in its crystalline peaks. The maximum intensity of the crystalline peaks can be obtained at a lower amount of clay which is 3 phr for unmodified-MMT and 1 phr for 2C18-MMT. This result indicates that the degree of crystallinity of the PET nanocomposite films increase with the addition of low amount of clay.

From these results it can be explained that the nanofiller; montmorillonite, can act as a nucleating agent for PET matrix at a few clay content resulting in higher degree of crystallinity compared with the pure PET film. Further increase in the amount of clay, the nucleating function of nanofiller will be loosed because of the clay agglomeration. These results are also related to the DSC analysis as will be discussed later.
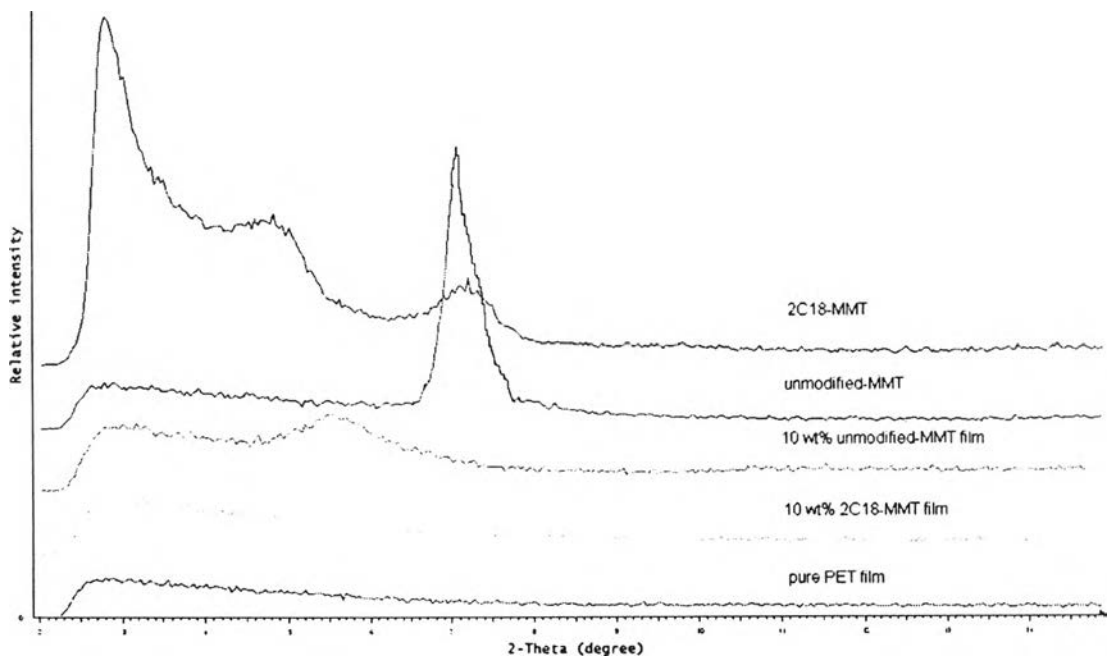

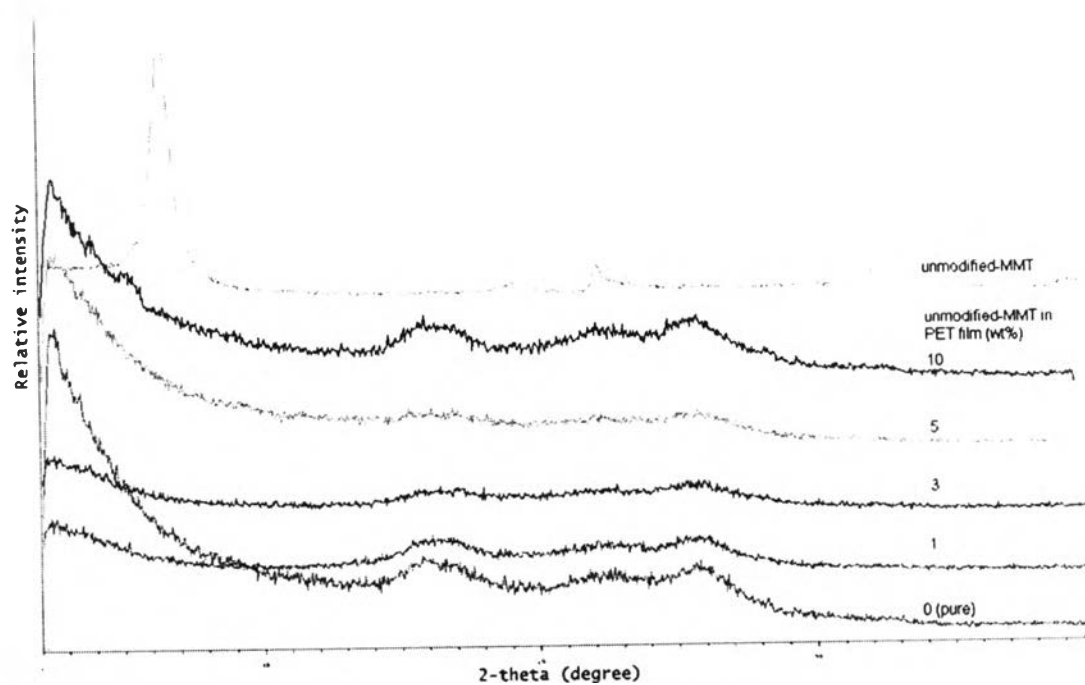Figure 4.3 The XRD patterns of clay, organoclay and PET/clay nanocomposite film.

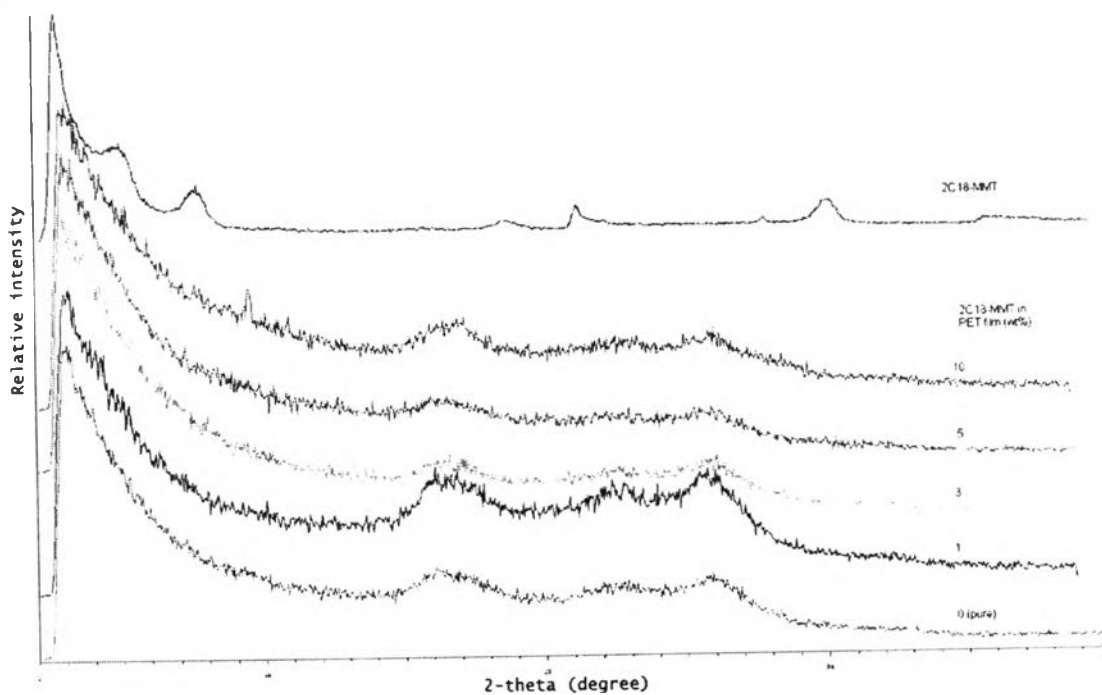Figure 4.4 The XRD patterns of unmodified –MMT and its nanocomposite films.

Figure 4.5 The XRD patterns of 2C18 –MMT and its nanocomposite films.

4.1.2.2 SEM

The scanning electron micrographs of 5%, 7%, and 9% PET nanocomposite films containing 2 types of clay at various concentration were shown in Figure 4.6, 4.7, and 4.8, respectively.

Considering at the PET concentration, the SEM micrograph shows no significant difference among each PET concentration. As seen in Figure 4.6, 4.7, and 4.8, the micrograph reveals that the effect of clay type also shows no significant difference on SEM analysis. However, the different clay content in polymer matrix has an effect on film morphology. From these results, it can be observed that when increasing the amount of clay, the PET matrix seems to be more homogeneous. The void which clearly seen in neat PET films, at every PET concentration, tends to disappear when increasing the amount of clay. This phenomenon can be explained by the nucleating effect of montmorillonite on PET/MMT nanocomposite that, generally, the neucleating agent would induce the polymer chain to reorder or to initiate crystal structure resulting in the dense polymer chain structure.

However, the SEM analysis did not show how nanofiller disperse in the polymer matrix due to the limitation of SEM itself. Further investigated by transmission electron microscopy (TEM) should be carried out.
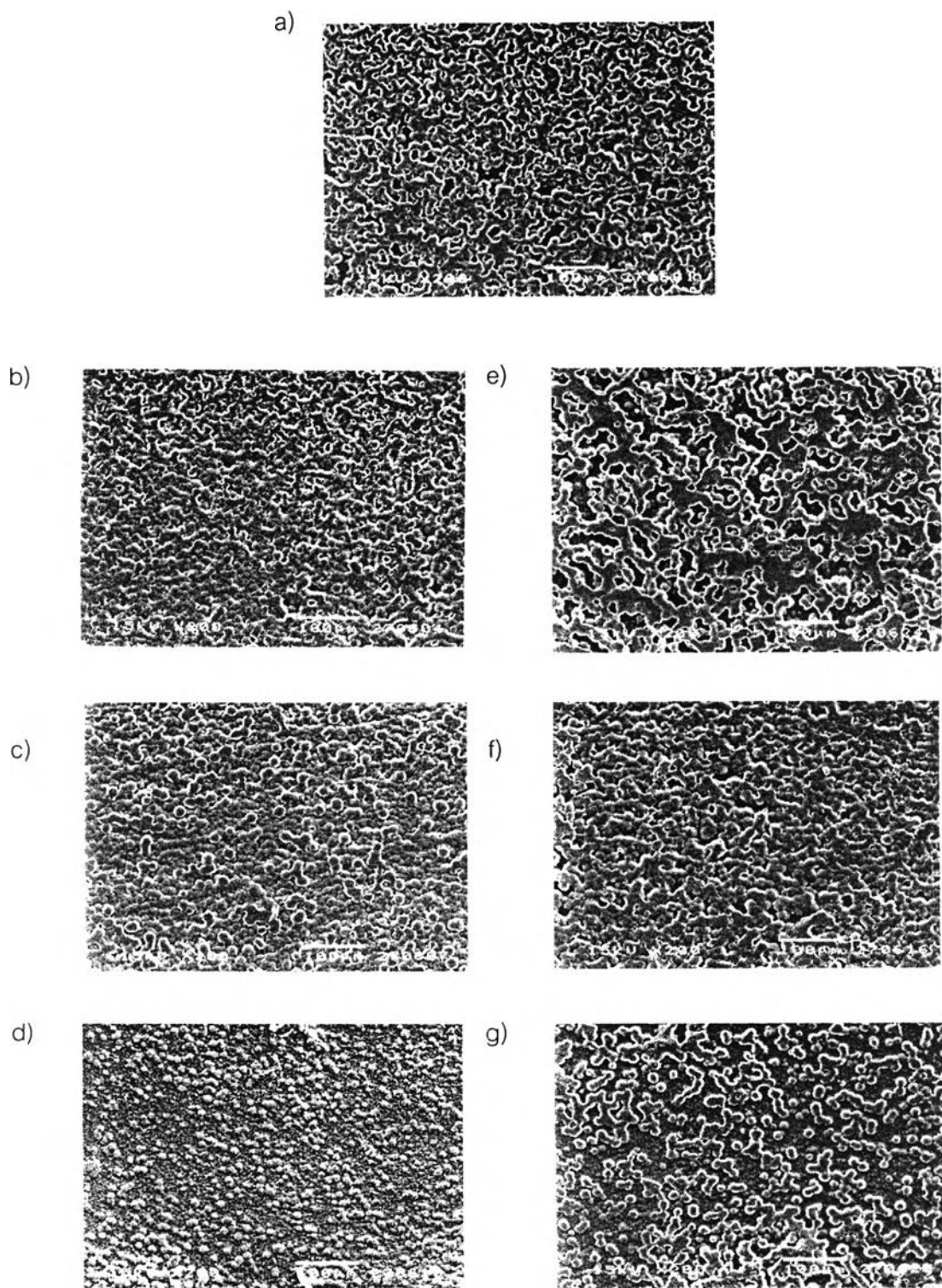
Figure 4.6   SEM micrographs of 5% PET and its nanocomposite films containing
             a) 0 phr, b) 1 phr, c) 3 phr, d) 5 phr of unmodified-MMT and e) 1 phr, f) 3
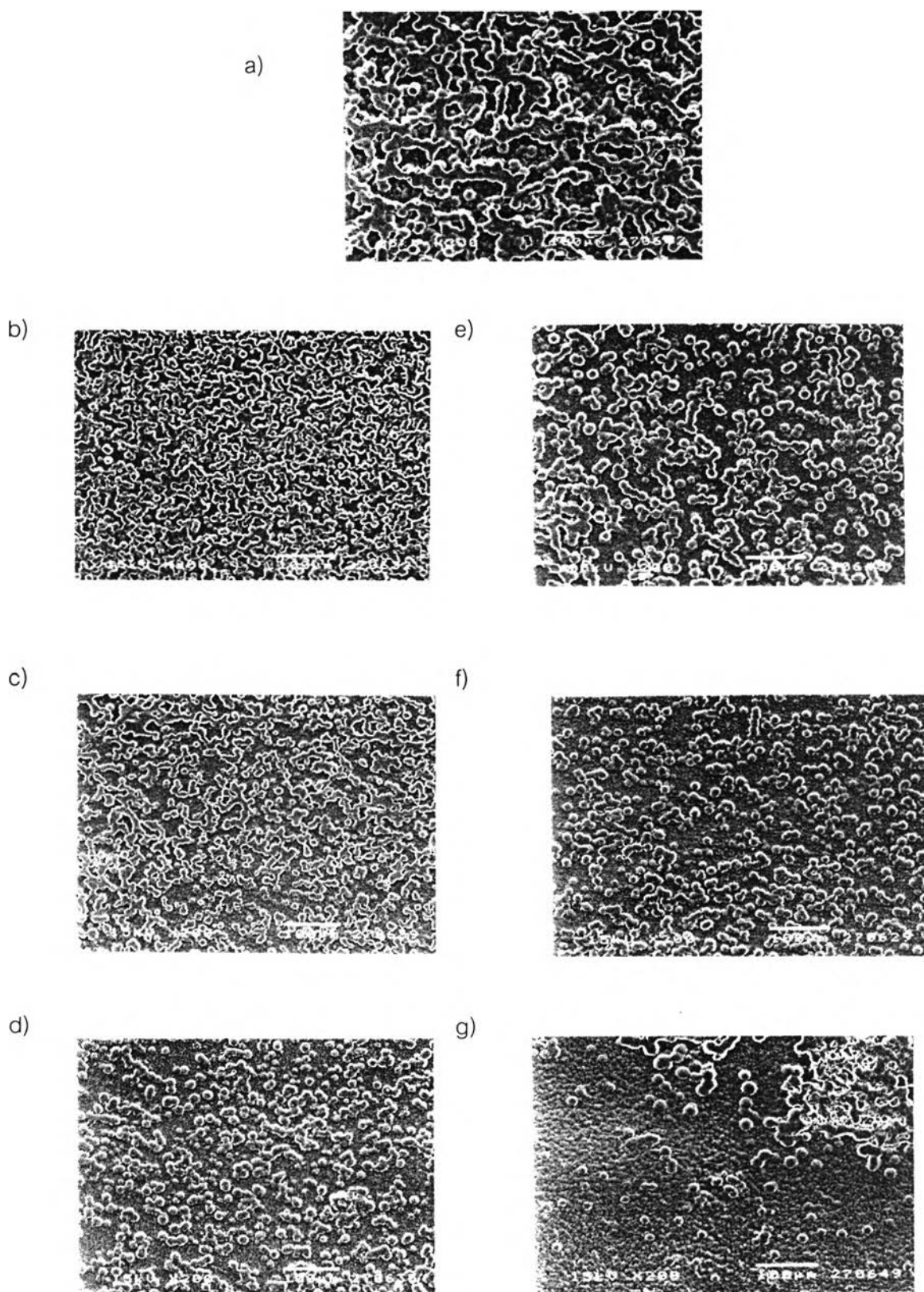   phr , g) 5 phr of organoclay

Figure 4.7 SEM micrographs of 7% PET and its nanocomposite films containing a) 0 phr, b) 1 phr, c) 3 phr, d) 5 phr of unmodified-MMT and e) 1 phr, f) 3 phr , g) 5 phr of organoclay
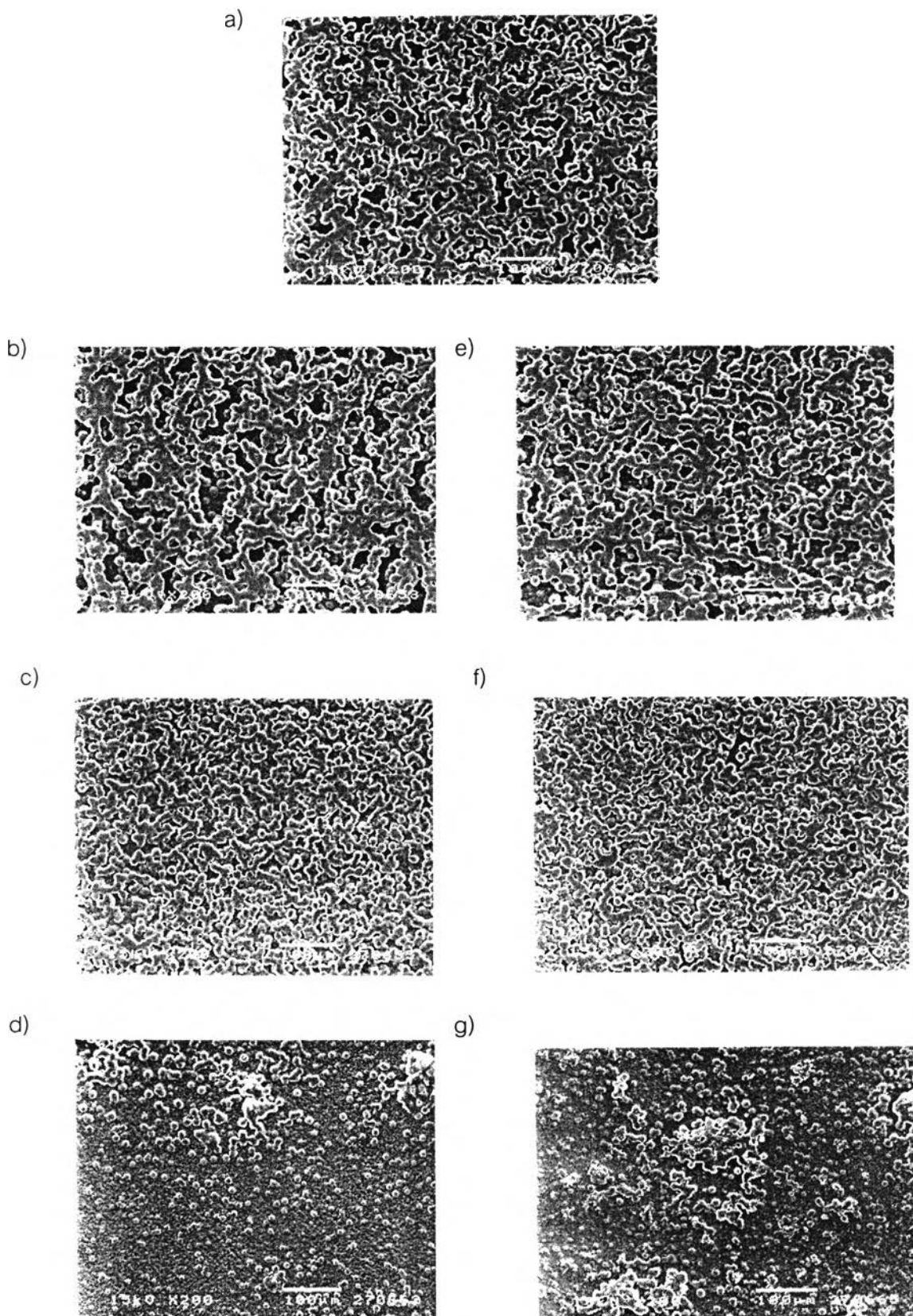
Figure 4.8 SEM micrographs of 9% PET and its nanocomposite films containing
a) 0 phr, b) 1 phr, c) 3 phr, d) 5 phr of unmodified-MMT and e) 1 phr, f) 3
phr , g) 5 phr of organoclay

4.1.3 Physical Appearance: Transparency

Transparency of packaging film is one of the aesthetic factors enhancing general appearance and customer acceptance. Generally, transparency of the film would be decreased when adding the micro particles in the film unlike the result from the film adding nanoparticles. The transparency of PET and its nanocomposite films were analyzed by UV/Vis spectroscopy. The % transmission of 7% PET and its nanocomposite films containing various amount of clay is presented in Figure 4.9. And the % transmittance values at 630 nm of PET and all PET nanocomposite films were shown in Table 4.2
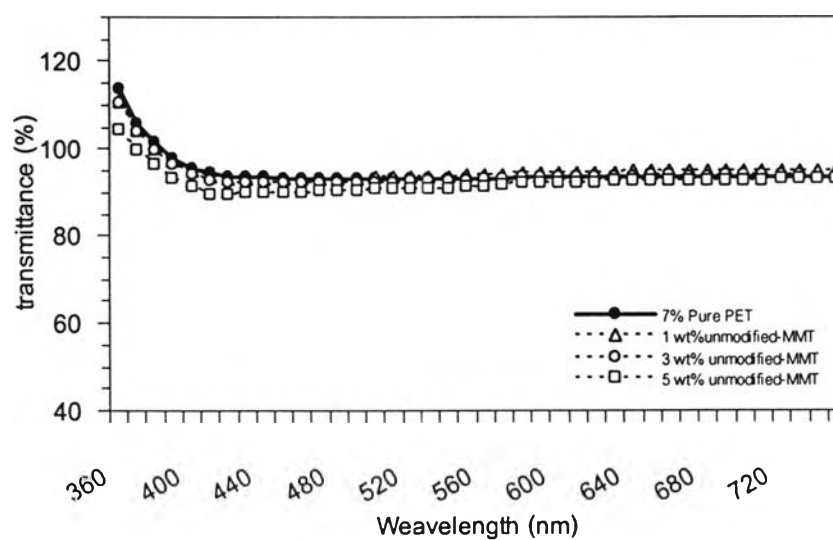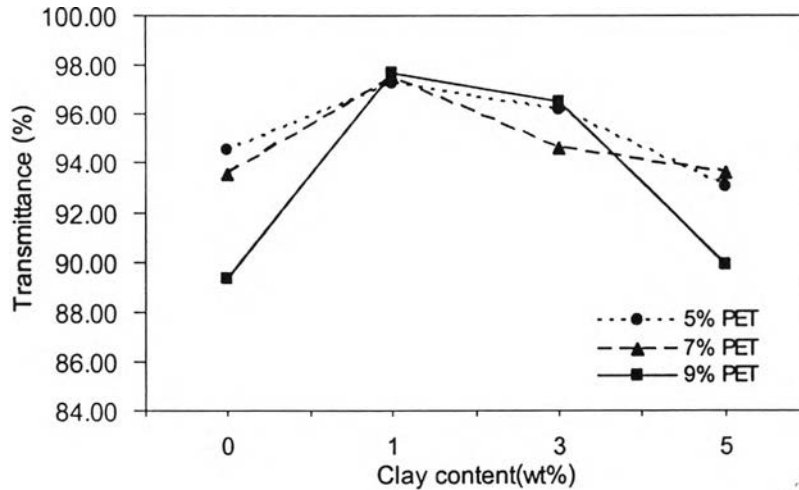

(a) unmodified-MMT
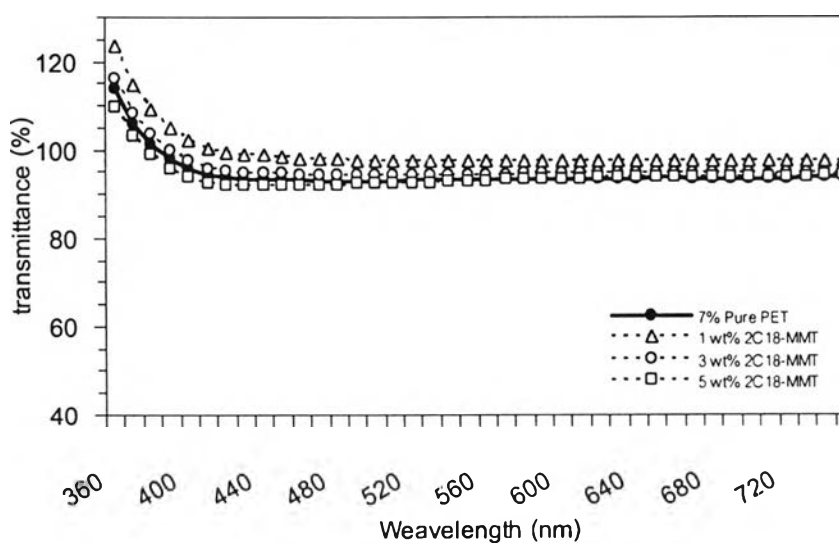
(b) organoclay

Figure 4.9 The effect of clay: unmodified-MMT (a), and organoclay (b) on transmittance spectrum of PET and its nanocomposite films at 7% PET.

Figure 4.10 (a) and (b) show the effect of PET concentration on % transmittance values of PET and its nanocomposite films containing various amount of unmodified-MMT and 2C18-MMT, respectively. It can be seen that, the % transmittance of pure PET films decreases when increasing the PET concentration. The % transmittance is highest at 5% PET and lowest at 9% PET. However, when adding the clay into the PET films, the % transmittance values of PET nanocomposite films clearly increase. Moreover, at 1 and 3 phr of both clay types, the 9% PET nanocomposite films have highest % transmittance values which are increased up to 97.73 and 97.65% for the films containing 1 phr unmodified-MMT and 2C18-MMT, respectively. From this result, it can be observed that the PET concentration has been related to the degree of clay's single layer disperses in PET matrix as will be discussed later.

Considering the effect of clay content, as seen in Figure 4.11, it was found that when increasing the clay content up to 1 phr, the % transmittance dramatically increases. For example, the % transmittance values of 7% PET films contained 1 phr unmodified-MMT and 2C18-MMT are 94.70 and 97.49 %, respectively, whereas that of neat PET film is 94.55 %. It can be explained that the film transparency depends on light transmission, which is related to the particle size of clay dispersion in PET matrix. According to the DSC characterization as will be discussed later reveals that the dispersed silicate layer acts as a nucleating agent which induces the fine crystal distributed in PET matrix. That phenomenon affected the transparency of nanocomposite film because the smaller crystals size than the wavelength of visible light (360-750 nm) allow light pass-through without any scattering. Moreover, the fine crystal would also enhance the mechanical properties of film which will be discussed shortly. Further increase in the clay content up to 5 phr , the % transmittance decreases. For example, at 7% PET contained 2C18-MMT films, the % transmittance values of neat PET, 1 phr, 3 phr, and 5phr clay are 93.51, 97.49, 94.61, and 93.58, respectively. One reason for this result may be explained that the increasing of clay content leads to an agglomeration of clay particle which has longer size than the wavelength of applied light leading to the hazy or cloudy nanocomposite films.

Table 4.2 % Transmittance value at 630 nm of PET and its nanocomposite films

| Formula	Sample Code	PET (%w/v)	MMT (phr)	organoclay (phr)	% Transmittance (at 630 nm)
1	5PET-0	5	-	-	93.51
2	5PET-A1		1	-	96.92
3	5PET-A3		3	-	96.07
4	5PET-A5		5	-	95.66
5	5PET-B1		-	1	97.22
6	5PET-B3		-	3	96.18
7	5PET-B5		-	5	93.05
8	7PET-0	7	-	-	94.55
9	7PET-A1		1	-	94.70
10	7PET-A3		3	-	93.74
11	7PET-A5		5	-	92.58
12	7PET-B1		-	1	97.49
13	7PET-B3		-	3	94.61
14	7PET-B5		-	5	93.58
15	9PET-0	9	-	-	89.34
16	9PET-A1		1	-	97.73
17	9PET-A3		3	-	96.28
18	9PET-A5		5	-	92.89
19	9PET-B1		-	1	97.65
20	9PET-B3		-	3	96.56
21	9PET-B5		-	5	89.85

(a) unmodified-MMT
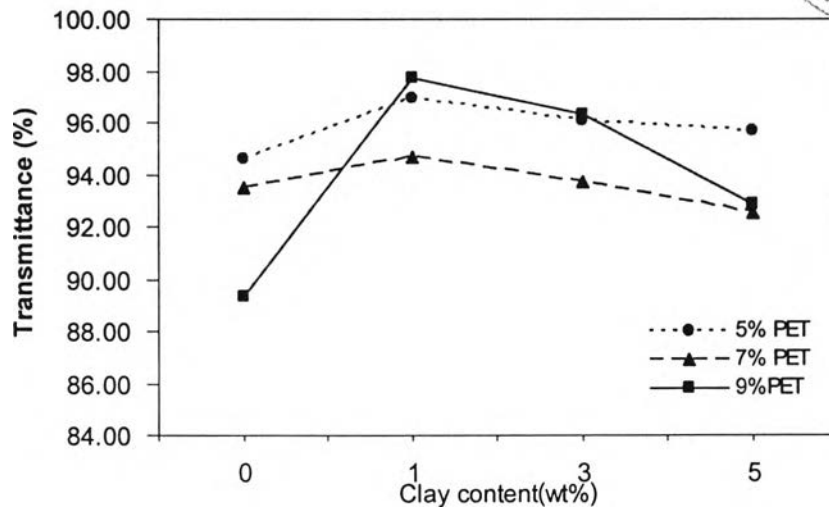
(b) organoclay

Figure 4.10 The effect of PET concentrations on % Transmittance values of PET and
its nanocomposite films containing various amount of (a) unmodified-MMT
and (b) organoclay

Comparing between unmodified-MMT and 2C18-MMT, it can be seen that
both clays have similar effect on % transmittance of nanocomposite films as seen in
Figure 4.10and 4.11 that % transmittance increases after the adding of 1 phr clay and
then decreases afterwards. However, as shown in Figure 4.11 the % transmittance
values of 2C18-MMT nanocomposite films are slightly higher than those of unmodified-
MMT nanocomposite films, excepted for 5%PET film contained 5 phr clay and 9%PET

film contained 1 and 5 phr clay. It can be explained by the fact that the organoclay, montmorillonite modified by dioctadecyl dimethyle ammonium, would be more compatible with the PET matrix than that unmodified one. Because the molecular structure of organoclay is more hydrophobic, like the PET matrix, compared with the unmodified or as-received montmorillonite which is high water affinity (hydrophilic). The ability to form homogeneous phase increases. Moreover, the modification of clay affects the long distance of d-spacing between each single layer. This extends the opportunity of exfoliation (delamination). This result is in good agreement with the XRD result.
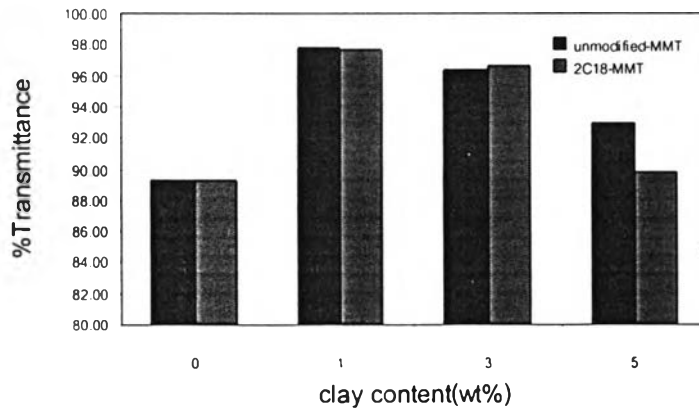
From these results, it can be concluded that the PET nanocomposite film achieves the highest transparancy at 1 phr of 2C18-MMT at all various PET concentrations. These results were in good agreement with the results from other characterization techniques as DSC and XRD.
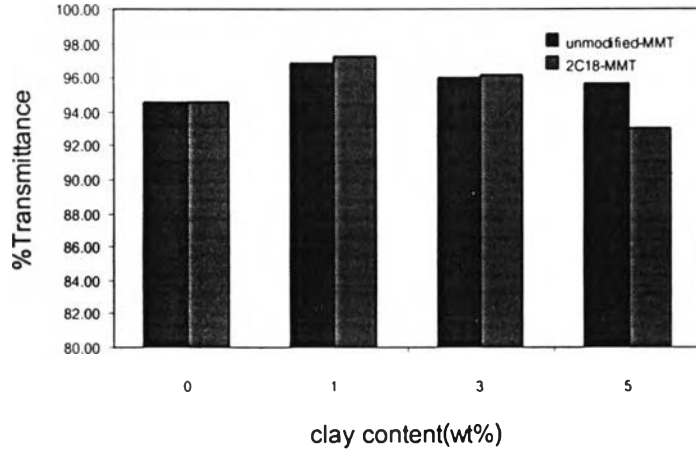
(a) 5%PET and its nanocomposites
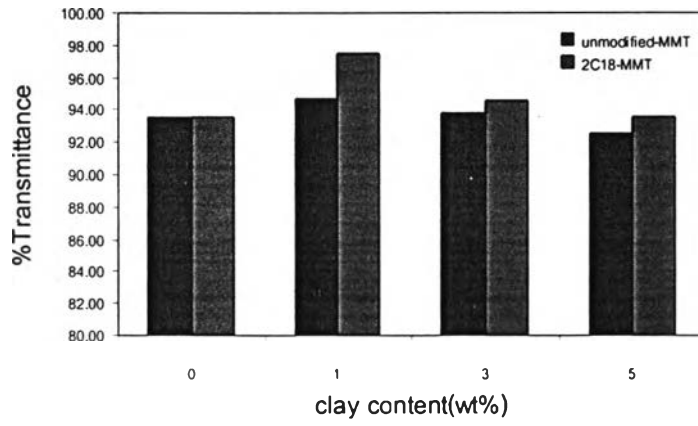
(b) 7%PET and its nanocomposites

(c) 9%PET and its nanocomposites

Figure 4.11 The effect of clay type on % Transmittance values of PET and its
nanocomposite films at (a) 5% (b) 7% and (c) 9% PET concentration.

4.1.5 Water Absorption

The water absorption of PET and its nanocomposite films was tested according to ASTM D570-98, using twenty four hours immersion method. However, the water absorption isotherms of PET and its nanocomposite films were plotted as a function of time for 14 days in order to obtain their equilibrium state.

The water absorption values of PET and its nanocomposite films were summarized in Table 4.3.

Table 4.3 The % water absorption of PET and the nanocomposites films

Formula	Sample Code	PET(%w/v)	nonmodified-MMT (phr)	organoclay (phr)	Water absorption (%)[a]		
					1 day	2 days	14 days
1	5PET-0	5	-	-	1.38	1.25	1.25
2	5PET-A1		1	-	0.53	0.55	0.64
3	5PET-A3		3	-	1.02	0.79	0.68
4	5PET-A5		5	-	1.10	1.32	1.09
5	5PET-B1		-	1	0.52	0.71	0.55
6	5PET-B3		-	3	0.19	0.53	0.43
7	5PET-B5		-	5	1.17	0.83	0.83
8	7PET-0	7	-	-	1.12	1.09	0.95
9	7PET-A1		1	-	0.62	0.62	0.73
10	7PET-A3		3	-	0.23	0.74	0.85
11	7PET-A5		5	-	1.04	1.33	1.42
12	7PET-B1		-	1	0.40	0.45	0.33
13	7PET-B3		-	3	0.64	0.81	0.61
14	7PET-B5		-	5	0.51	1.16	1.06
15	9PET-0	9	-	-	1.21	1.37	1.27
16	9PET-A1		1	-	0.74	0.63	0.62
17	9PET-A3		3	-	0.51	1.09	1.09
18	9PET-A5		5	-	0.81	1.68	1.87
19	9PET-B1		-	1	0.63	0.62	0.62
20	9PET-B3		-	3	0.11	0.62	0.83
21	9PET-B5		-	5	0.76	0.77	0.77

[a] the mean values of %water absorption

Figure 4.12 graphically shows the water absorption isotherms of PET and its nanocomposite films containing two types of MMT at various content. The results reveal that both unmodified-MMT and organoclay content has great effect on the % water absorption. It can be seen that the ability to absorb water of PET and its nanocomposite film increases with increasing exposure time. Their water absorption isotherms initially show a linear relationship between water uptake and time, followed by saturation. As shown, the amount of absorbed water decreases with the addition of clay particles, in particular the 2C18-MMT. The effect of each investigated variables are discussed as follows.

The effect of PET concentration on the % water absorption is demonstrated in Figure 4.13. The results from Table 4.3 and Figure 4.13 show that the % water absorption tends to increase when increasing the PET concentration. For example, at 3 phr organoclay nanocomposite film, the water absorption values at 5%, 7%, 9% PET are 0.43%, 0.62%, 0.83%, respectively. It can be realized that the PET concentration has an effect on water absorption of PET/MMT nanocomposite films due to the dispersion of clay platelet in PET matrix. It can be explained that when increasing the PET concentration, the density of polymer chain would be higher. Thus, the opportunity of intercalation between polymer chain and clay platelet would be decreased. Moreover, clay agglomeration may be affected on the water absorption ability of PET nanocomposite films, as will be discussed as follows.

Considering the effect of clay type, Figure 4.14 shows the effect of clay type on % water absorption at various PET concentration. It is seen that organoclay had more pronounced effect on the water absorption of the nanocomposite films than the unmodified-MMT. The organoclay/PET nanocomposite films have lower water absorption values than the unmodified-MMT/PET nanocomposite films. As listed in Table 4.3, for example, at 7 %w/v PET after 14 days of subjecting the films in the water, the % water absorption values of nanocomposite films containing 1, 3, 5 phr of unmodified-MMT are 0.73, 0.85 and 1.42, respectively, whereas those values of the organoclay nanocomposite films are 0.33, 0.61 and 1.06 respectively. It can be explained that the organoclay which was modified with dioctadecyl dimethyl ammonium (2C18-MMT) is more hydrophobic compared to an unmodified-MMT. In other words, 2C18-MMT has

lower polar group than the unmodified-MMT, hence, the % water absorption of organoclay nanocomposite films has lower than that of unmodified-MMT.

The effect of clay content on PET nanocomposite films is also clearly seen in Figure 4.14 that the water absorption values decrease compared to the neat PET film. However, when increasing the clay content, the water absorption of the nanocomposite films linearly increases.

The lower % water absorption would be received at lower clay content (1-3 phr). However, at 5 phr of clay, the % water absorption of some formula, 7% PET/unmodified-MMT, 7%PET/organoclay, and 9%PET/unmodified-MMT, is much higher than that of the neat PET film. For example, at 9 %w/v PET after 14 days of subjecting the films in the water, the % water absorption values of nanocomposite film containing 1%, 3%, 5% of unmodified-MMT are 0.62 ,1.09 and 1.87, respectively, whereas this value of the neat PET film is 1.27.

These results can be described by the effect of polar groups. It is well known that the polymer matrix contained more polar groups tends to have higher water sportive affinity. However, the accessibility of the polar groups and the relative strength of the water-water interaction vs. the water-polymer interaction are both important. [12] The silicate layer which dispersed in polymer matrix tends to reduce the accessibility of the polar groups of PET. Therefore, better clay dispersion should possess lower water absorption. However, upon increasing the amount of clay, the water absorption of nanocomposite films increase. This result is probably attributed to the degree of crystallinity (χ_c) of nanocomposite films. As will be discussed in the DSC analysis, at lower amount of clay (1-3 phr), the nanocomposite films have higher degree of crystallinity due to the nucleating effect of montmorillonite, compared to the neat PET film. Therefore, it is difficult for water molecule to enter into the film structure. However, at higher clay content (5 phr), the degree of crystallinity of nanocomposite films decreases because of an agglomeration of clay particles. As a result, water molecules can be easily absorbed into the amorphous structure of the films. Besides the degree of crystallinity, we can also describe the decrease in water absorption upon the addition of clay particles obstruct the passage of water molecules though the PET matrix; hence the water absorption of nanocomposite film decrease.

Related to the results from SEM annlysis, the surface morphology of nanocomposite films was observed to be more compatible when increasing the clay content. The voids were reduced so the water can hardly absorb into the PET nanocomposite films. It can be concluded that the PET nanocomposite film at suitable PET concentration (7 %w/v), containing organoclay at lower clay content (recommended 1 phr) is the best for water barrier property; when the clay content exceeds 5 phr, its % water absorption is already higher than that of the neat PET film.
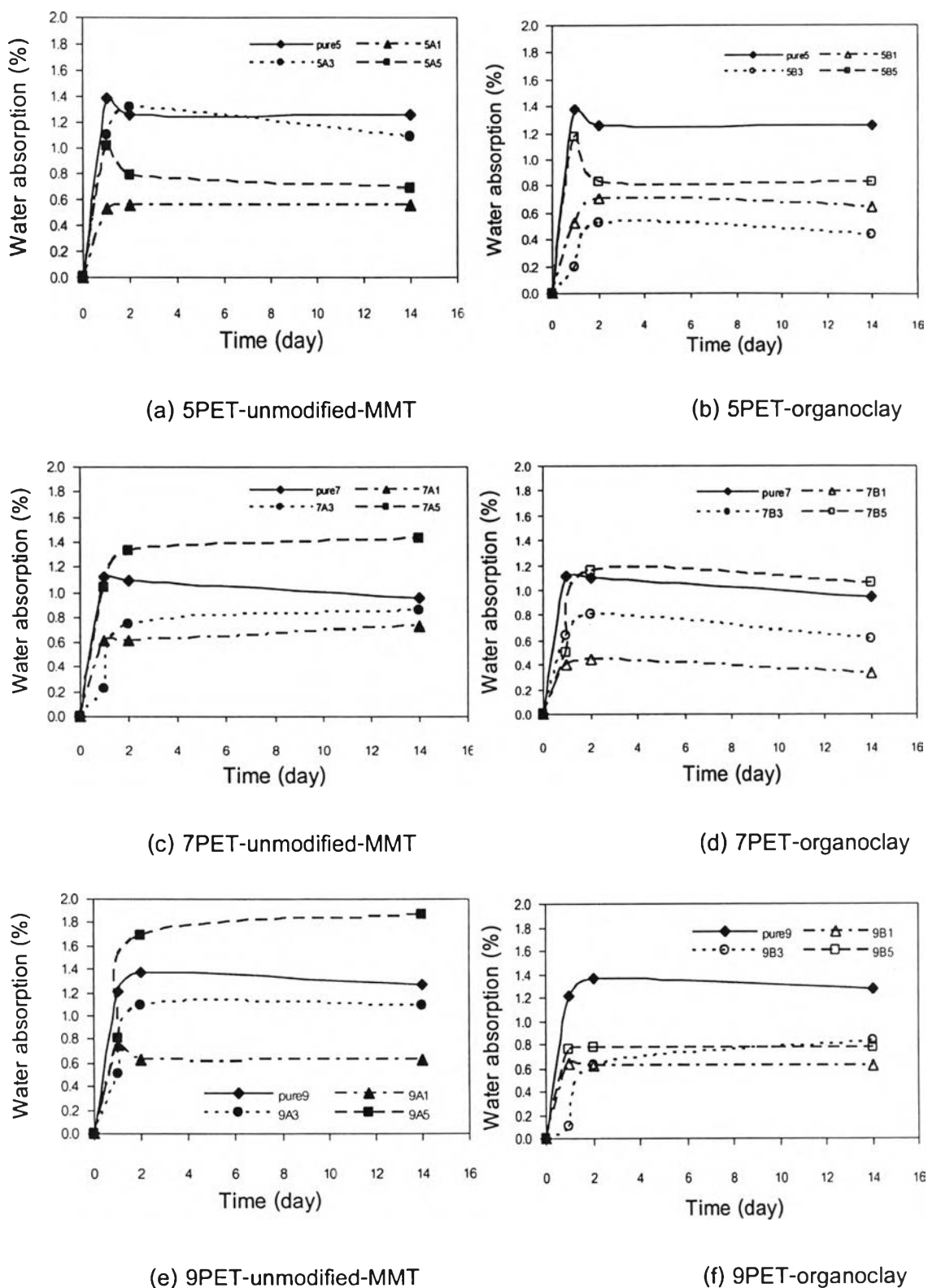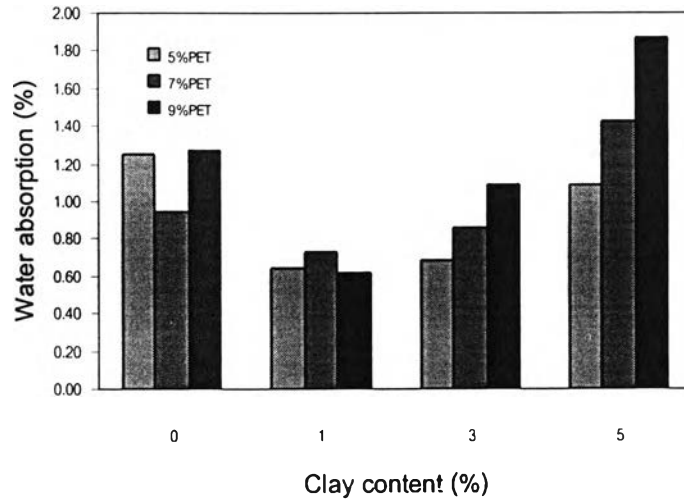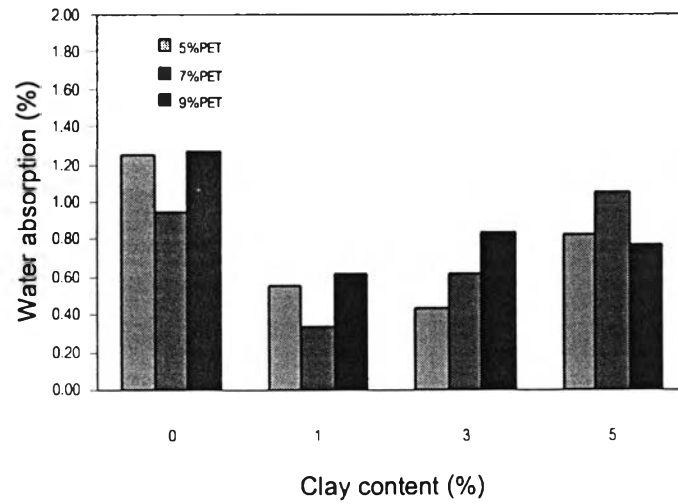
(a) 5PET-unmodified-MMT

(b) 5PET-organoclay

(c) 7PET-unmodified-MMT

(d) 7PET-organoclay

(e) 9PET-unmodified-MMT

(f) 9PET-organoclay

Figure4.12 The effect of clay type and clay content on water absorption isotherms of
PET and its nanocomposite films at various PET concentrations: 5% (a,b),
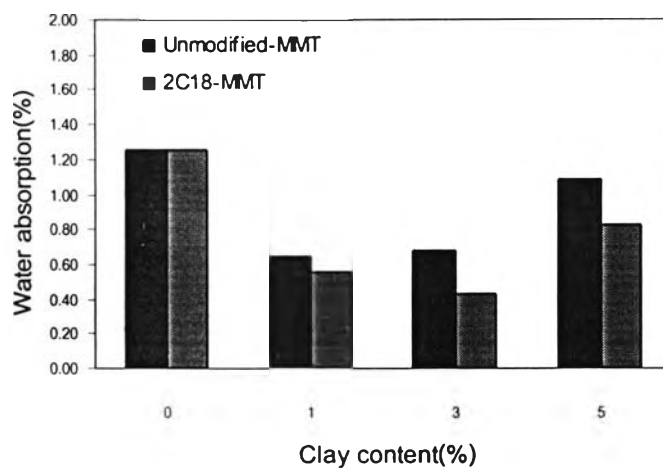7%(c,d),and 9%(e,f) PET concentration
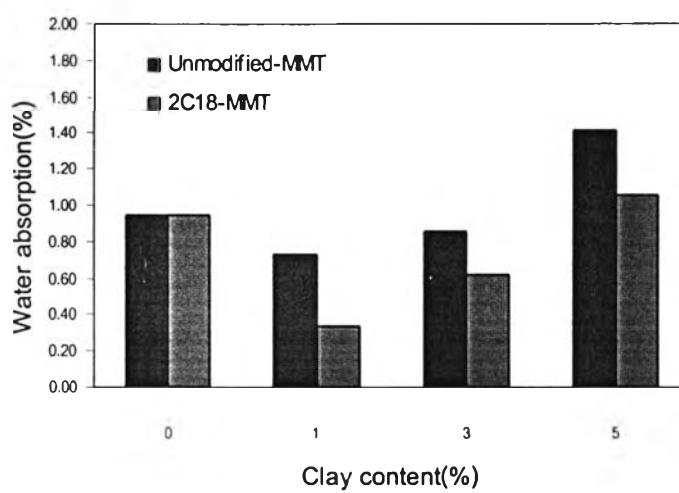
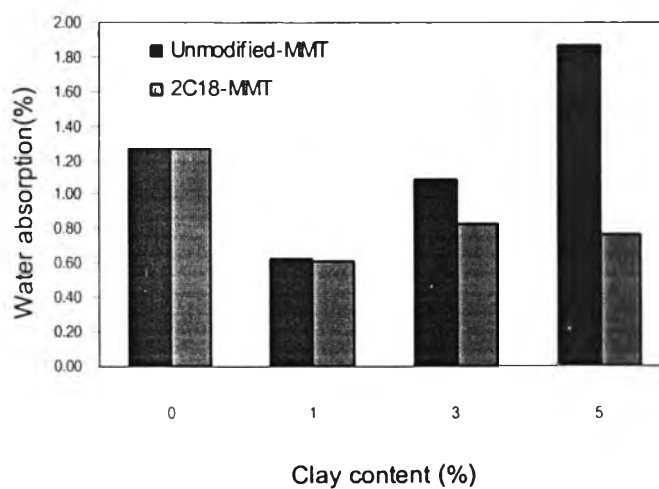(a) unmodified-MMT

(b) organoclay

Figure 4.13 The effect of PET concentrations on the % water absorption of PET and its nanocomposite films containing (a) unmodified-MMT and (b) organoclay

(a) 5% w/v PET

(b) 7% w/v PET

(c) 9% w/v PET

Figure 4.14 The effect of clay type on % water absorption of PET and its

nanocomposite films at (a) 5 %, (b) 7%, (c) 9% w/v PET concentration

4.2 Mechanical Properties Characterization : Tensile Properties Evaluation

The tensile properties including tensile strength, Young's modulus, and percent elongation at break were investigated by universal testing machine, according to ASTM D 882-02.

In this work, the mechanical properties in both machine direction (MD) and transverse direction (TD) were tested. Due to the film formation, auto film applicator has applied load on to the film during casting, in particular in the machine direction. Therefore, it has been assumed that the mechanical properties in each direction would be different. However, the results on tensile properties of both MD and TD are not significantly different. So, the tensile properties in MD will only be presented here in this chapter. All results in both MD and TD were reported in an appendix C.

The tensile properties of pure PET and its nanocomposite films are listed in Table 4.4.

Figure 4.15 and 4.16 show the effect of PET concentration on the tensile strength and Young's modulus of nanocomposite films, respectively. From these results, it can be seen that at 0 phr clay content the tensile strength and Young's modulus increase with increasing the concentration of PET. It may be explained that when increasing the PET concentration, the number of polymer chain and the polymer chain entanglement increase, and hence the grater amount of force is needed to break those entanglement.

The effect of clay types on tensile strength and Young's modulus of nanocomposite films is also shown in Figure 4.15 and 4.16, respectively. Obviously compared with 2C18-MMT nanocomposite films, the tensile strength of unmodified-MMT nanocomposite films is lower, especially at maximum values. For example, at 7% PET, the tensile strength values of PET film containing 1, 3, 5 phr unmodified-MMT are 2.23, 3.83 and 2.36 MPa, respectively, whereas those values for 2C18-MMT/PET nanocomposite films are 3.36, 5.84, and 4.54, respectively. Similarly, as shown in Table 4.4, the Young's modulus of 2C18-MMT nanocomposite films is higher than that of the unmodified-MMT nanocomposite films. The higher efficiency of 2C18-MMT can be

explained by the better polymer intercalation reached with ion exchange reaction of clay in comparison with unmodified material (as evidenced by XRD measurement).

Table 4.4 Tensile properties of pure PET and its nanocomposite films

| PET (%w/v)	Unmodified-MMT (phr)	organoclay (phr)	Tensile Properties		
			Ult. Strength (MPa)	Young's Modulus (MPa)	E.B (%)[a]
5	-	-	2.06	403.57	0.58
	1	-	2.37	537.28	0.46
	3	-	2.25	414.63	0.39
	5	-	1.33	302.74	0.27
	-	1	3.49	653.27	0.42
	-	3	1.42	341.97	0.17
	-	5	0.94	347.24	0.12
7	-	-	2.144	496.71	0.32
	1	-	2.23	467.44	0.34
	3	-	3.83	589.24	0.35
	5	-	2.36	534.56	0.32
	-	1	3.36	714.74	0.35
	-	3	5.84	895.35	0.35
	-	5	4.54	526.00	0.35
9	-	-	3.49	575.75	0.65
	1	-	3.55	605.48	0.61
	3	-	2.79	446.74	0.47
	5	-	2.21	478.09	0.32
	-	1	3.06	591.86	0.42
	-	3	4.41	839.76	0.51
	-	5	2.57	556.55	0.41

[a] Elongation percent at break
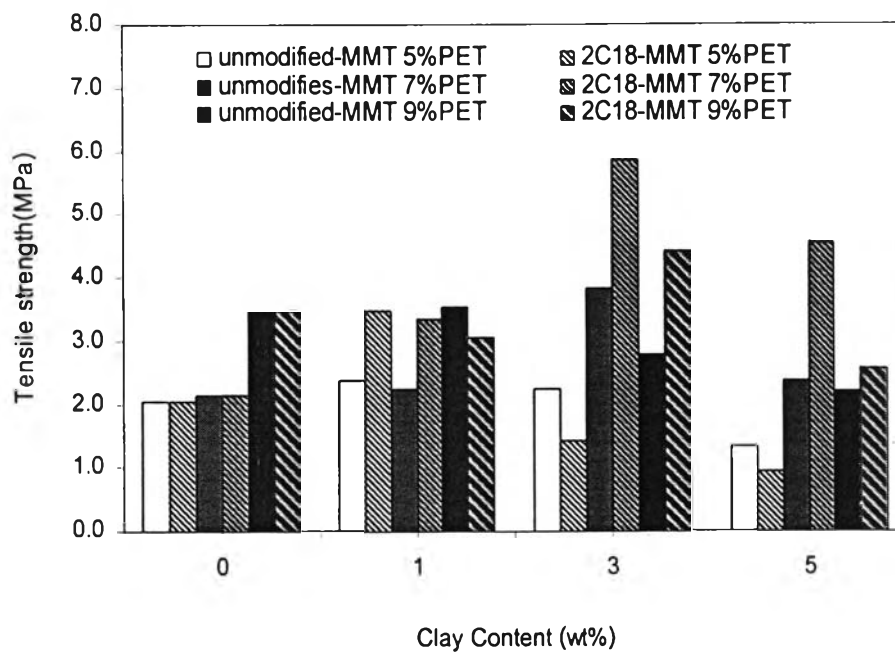
Figure 4.15 Effect of clay content on the tensile strength of the nanocomposite films at various PET concentrations.
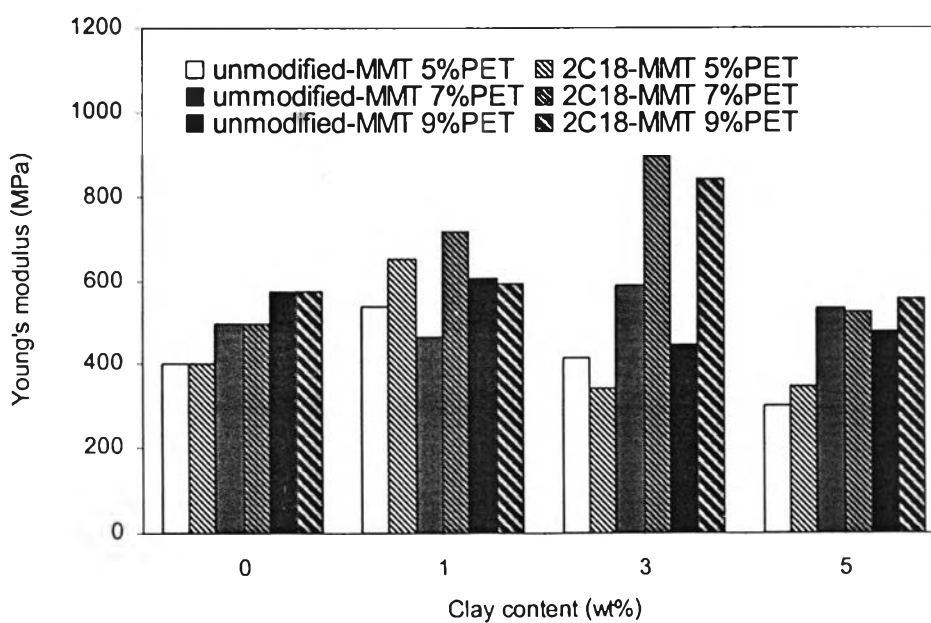

Figure 4.16 Effect of clay content on the Young's modulus of the nanocomposite films at various PET concentrations.

Figure 4.15 and 4.16 also show the effect of clay content on tensile properties. The effect of montmorillonite was found to enhance as well as impair the tensile properties depending on the amount of added clay. At low montmorillonite content, approximately 1-3 phr, depending on the PET concentration, an increase in clay content resulted in an increase effect on the tensile strength and Young's modulus. For example, at 5 %w/v PET, the maximum tensile properties can be obtained at 1 phr clay, whereas at 7%w/v PET, the maximum tensile properties can be obtained at higher clay content which is 3 phr of both clay types. In addtion, their values are also greater than those at lower PET concentration. For example, the tensile strength of 3 phr unmodified-MMT and 2C18-MMT is 3.83 and 5.84 MPa, respectively, whereas those values for 5 % w/v PET films containing 1 phr unmodified-MMT and 2C18-MMT are 2.37 and 3.49, respectively. However, at 9 %w/v PET, the tensile properties of nanocomposite film contained unmodified-MMT and 2C18-MMT reached its maximum values at 1 phr and 3 phr, respectively. A further increase in clay content upto 5 % led to an adverse effect on the tensile properties as evidenced by a decrease in both tensile strength and Young's modulus.

From the above results, it can be concluded that the type and amount of clay have an effect on the tensile properties of the PET nanocomposite films. The addition of both types of clay can increase the strength and stiffness of the nanocomposite films upto a certain degree of clay content due to the reinforcement effect. It is well known that the mechanical properties of composites depend on many factors such size, shape, amount, including rigidity of the filler, the degree of dispersion of the filler in matrix resin, and the affinity with the matrix polymer. [19] The greatest dispersion will receive the great enhancement of composites properties. The introduction of nanoclay itself will help to increase the interface properties of polymer composites due to the intercalation and exfoliation structure. As we know the failure to disperse can induce agglomeration. Failure initiated many clay agglomerate which meant that cracks were initiated on and propagated inside the agglomerates, as described in other nanocomposite study. [10-11,53] Increasing the clay content leads to agglomeration of the clay particle which reduces the tensile strength and modulus of material. These results reflect that clay size and the particle dispersion or distribution is crucial factors affecting the mechanical

properties of typical composite materials including nanocomposite. In this work, at low clay content the dioctadecyl dimethyl ammonium could effectively intercalate into silicate layer, producing the nanocomposite with larger surface area due to gallery expansion. In addition, due to its compatibility with PET matrix, hence nanocomposite was easily dispersed, resulting in dispersion with good particle distribution. On the other hand, excess amount of clay was a likely cause of phase separation and poor particle distribution or agglomeration of clay which led to poor tensile properties as proven by the decrease in tensile strength and Young's modulus.

Figure 4.17 shows the effect of PET concentration, clay type and clay content on the percent elongation at break of PET nanocomposite films. Considering the effect of PET concentration, the percent elongation at break increases when increasing the PET concentration from 5 to 9 %w/v. It can be resulted from the increasing number of polymer chain which can increase the chain entanglement of PET molecules. This chain entanglement is assumed to have an effect on increasing the % elongation at break. Since when chain entanglement increases, it is usually required higher force to disentanglement of these molecules which affected to more load resistance.
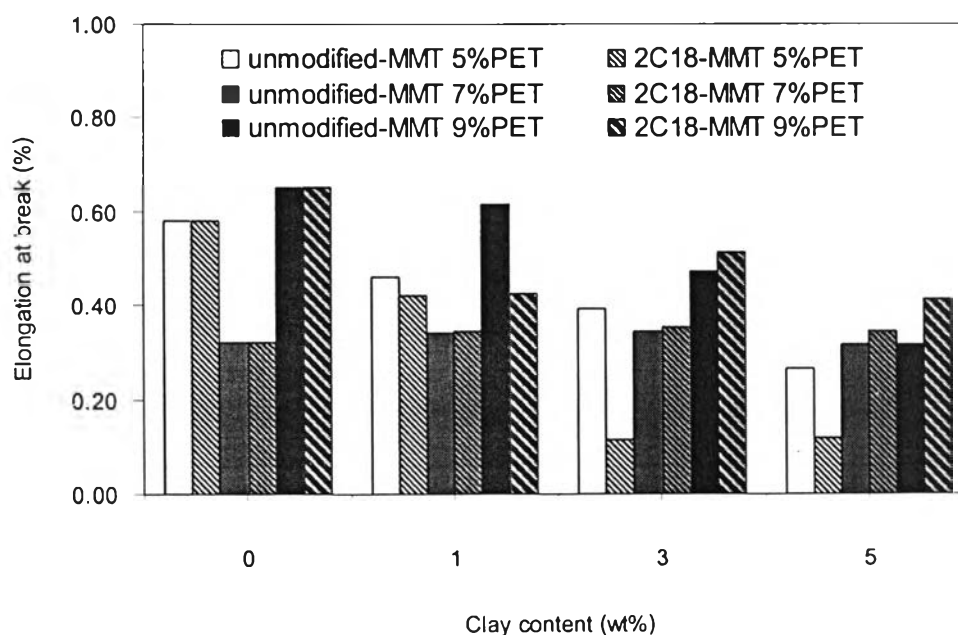

Figure 4.17 Effect of clay content on the elongation at break of the nanocomposite films at various PET concentrations.

Form the results, it can be seen that there is no significant difference in the % elongation at break between two types of clay whereas the amount of clay has dramatically effected on the percent elongation at break. The % elongation at break decreases when increasing the clay content of both clay types which is similar to the micro-structure composite. It can be explained that the decrease in % elongation at break is due to the natural rigidity of silicate-sheet nanofiller.

In summary, based solely on this work, the best tensile properties of PET/MMT nanocomposite film can be achieved from the 7%w/v PET film containing 3 phr of 2C18-MMT.

4.3   Thermal Properties Characterization

4.3.1   Thermogravimetric analysis (TGA)

Thermal stability of pure PET and its nanocomposite films is summarized in Table 4.5 and the TGA thermograms of various PET concentrations at 3 phr 2C18-MMT are shown in Figure 4.18.

The TGA thermograms of PET nanocomposite films show two step decompositions. The first step which is corresponding to the decomposition of residue solvent in the film samples is shown between $140\text{-}180^\circ C$ whereas the second step occurred between $417\text{-}443\,^\circ C$ is due to the major decomposition of PET. It can be seen that, at 3 phr clay, when increasing the PET concentration from 5 to 9 %w/v, T_d' clearly increases, in addition, the percent residual weight at $600\,^\circ C$ ($\%wt_R^{600}$) tends to increase when increasing the PET concentration. It can be resulted from increasing of polymer chain which can increase the heat used to decompose all of the sample related to the weight residua as well. In other word, the various of PET concentration may affect heat-resistance property. Due to the dispersion of clay in polymer matrix, it could be assumed that the chance of chain entanglement decreased at low PET concentration. So, the chance of chain in intercalation with clay layer would be increased. From this reason, the heat-resistance property would be increased; the explanation of this phenomenon which incorporated with clay type and clay content will be discussed later.

Table 4.5 Thermogravimetric analysis of PET and its nanocomposite films

Formula	Sample Code	PET (%w/v)	Unmodified-MMT (phr)	organoclay (phr)	$T_D^{i\ a}$ (°C)	$wt_R^{600\ b}$ (%)
1	5PET-0	5	-	-	429	5
2	5PET-A1		1	-	421	8
3	5PET-A3		3	-	422	13
4	5PET-A5		5	-	421	15
5	5PET-B1		-	1	421	8
6	5PET-B3		-	3	416	13
7	5PET-B5		-	5	416	14
8	7PET-0	7	-	-	420	5
9	7PET-A1		1	-	428	11
10	7PET-A3		3	-	423	13
11	7PET-A5		5	-	420	16
12	7PET-B1		-	1	423	11
13	7PET-B3		-	3	421	12
14	7PET-B5		-	5	420	13
15	9PET-0	9	-	-	421	9
16	9PET-A1		1	-	429	11
17	9PET-A3		3	-	424	15
18	9PET-A5		5	-	423	16
19	9PET-B1		-	1	429	13
20	9PET-B3		-	3	427	14
21	9PET-B5		-	5	422	16

[a] Initial weight reduction onset temperature

[b] Weight percent of residue at 600 °C

Figure 4.19 shows the TGA thermograms of unmodified-MMT and 2C18-MMT powder. The types of clay have an effect on the initial decomposition temperature of films. From these results, the T_d^i of 2C18-MMT nanocomposite films is lower than those of unmodified-MMT films. It can be attributed to the thermal stability of clay itself. As shown, the T_d^i of unmodified-MMT is higher compared with 2C18-MMT. In addition, it can be seen that the 2C18-MMT show steep decomposition curve due to the clay's modification with dioctadecyl dimethyl ammonium which has lower thermal stability

leading to the lower T_d' of 2C18-MMT nanocomposite films. The lower in the residue weight of the 2C18-MMT should be corresponded to the volatile decomposition product of dioctadecyl dimethyl ammonium.
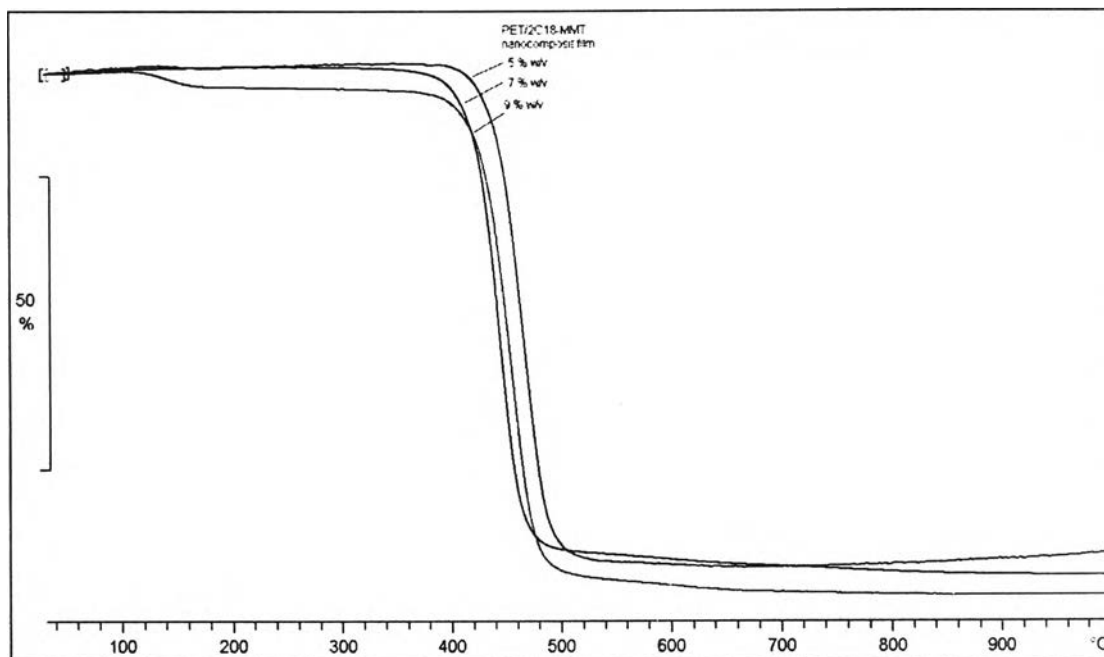

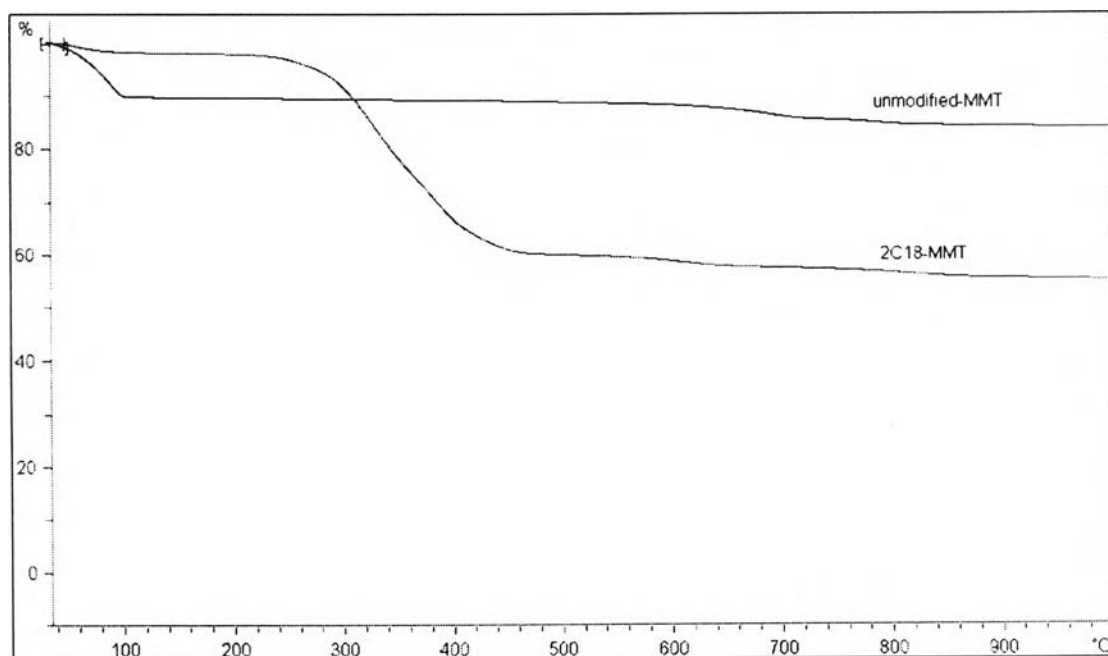Figure 4.18 TGA thermograms of various PET concentrations: 5%, 7%, and 9% at 3 phr 2C18-MMT

Figure 4.19 The TGA thermograms of unmodified-MMT and organoclay: 2C18-MMT

The TGA thermogram in Figure 4.20, 4.21 and 4.22 shows the effect of clay content on thermal properties. Considering at 7% and 9% w/v PET, the TGA thermograms of nanocomposite films contained both of clay types show the higher T_D^i compared with those of the neat PET Film. For example, The T_D^i of 7% PET, 7PETA1,7PETA3 and 7PETA5 is 420 , 428 , 423, and 420 °C, respectively, and the T_D^i of 7PETB1, 7PETB3, 7PETB5 is 423 , 421 ,and 420 °C, respectively. With increasing clay content, the T_D^i of nanocomposite films decreases. Nevertheless, the lowest T_D^i obtained at 5 phr clay are comparable to the T_D^i of pure PET films. Considering the above results, it is consistently believed that the introduction of inorganic components into organic polymer can improve their thermal stability on the basic of the fact that clay has good thermal stability, as good agreement with the previous research [14]. However, comparing between two types of clay it was found that the T_D^i of 2C18-MMT nanocomposite films is lower than those of unmodified-MMT nanocomposite films. It can be attributed to the higher thermal stability of unmodified-MMT itself, as shown in Figure 4.19. Moreover, the residue weight at 600°C (wt_R^{600}) of 7% w/v PET films linearly increases, ranging from 5-16% for clay content from 0 to 5 phr unmodified-MMT and 5-13 % for 2C18-MMT. This enhancement of char formation is ascribed to the high-heat resistance due to the clay itself. [11]. The results on thermal property of 9% w/v PET is also similar to 7% w/v PET, as shown in Figure 4.22 and Table 4.4.

On the other hand, at 5% PET, the T_D^i of nanocomposite film is lower than that of the neat PET film, as shown in Figure 4.20. The T_D^i of 5% PET, 5PETA1, 5PETA3 and 5PETA5 is 429,421,422, and 421 °C, respectively, and the T_D^i of 5PETB1, 5PETB3, 5PETB5 is 421,416, and 416 °C, respectively. However, similar to 7% and 9% w/v PET that the T_D^i of nanocomposite film tends to decrease with the clay content and the wt_R^{600} is also increases with the clay content. From these results, it can be explained by the other function of clay filler. The clay itself, beside the good thermal stabilizer, can also act as catalyst for the degradation of polymer matrix [54]. The organoclay which was modified with alkylammonium cation could suffer from the decomposition reaction following the Hofmann elimination reaction and its product would catalyze the degradation of polymer matrix [55]. This catalyst effect would reduce the thermal stability of polymer/clay nanocomposite [11].

Nevertheless, the enhancement of nanocomposite's thermal stability is probably due to the barrier effect of silicate layer and char on oxygen permeability. It can be assumed to the hindered diffusion of volatile decomposition product within the composite that can be explain by Neilson's tortuous path model in which the platelets obstruct the passage of gases and other permeates through the polymer matrix. The Fully dispersed silicate layers in polymer matrix lead to a longer pathway which the gases or other permeates pass through the polymer matrix. This is also due to the large aspect ratio of silicate single layer. If the clay starts to agglomerate (excess clay loading), they will less the large aspect ratio which leads to on shorter pathway, as also introduce in chapter II.
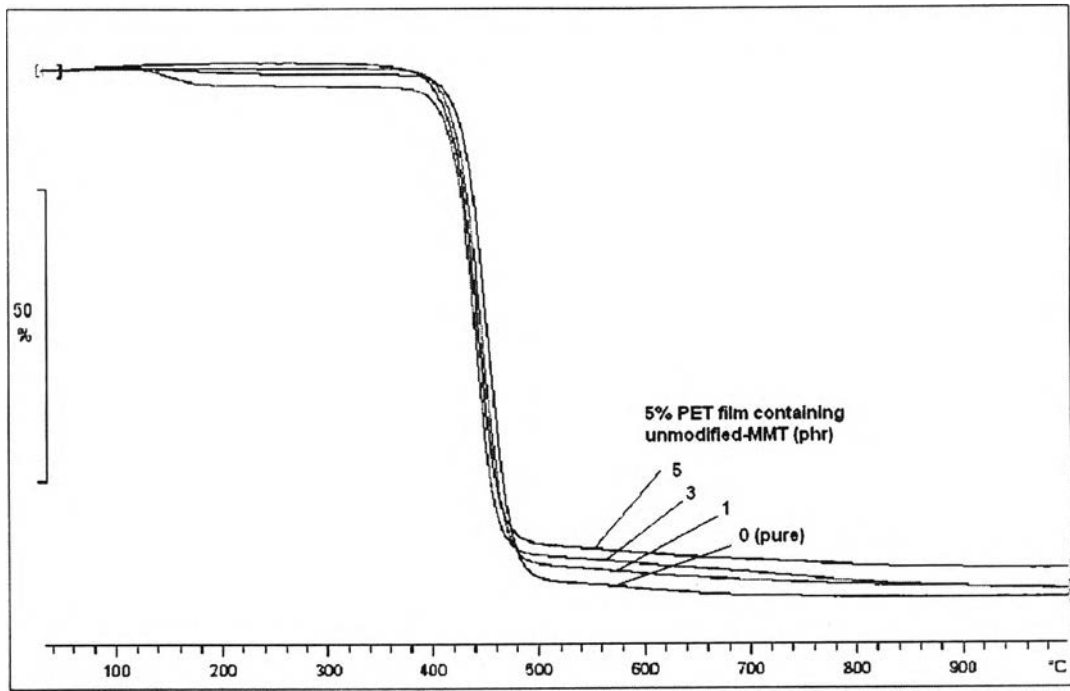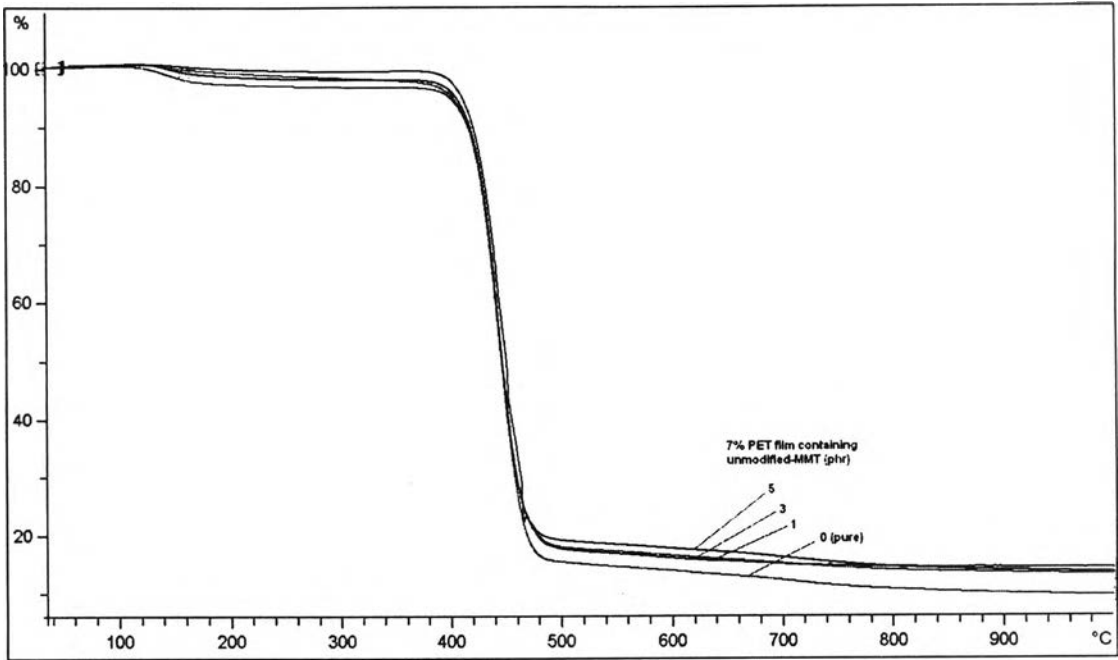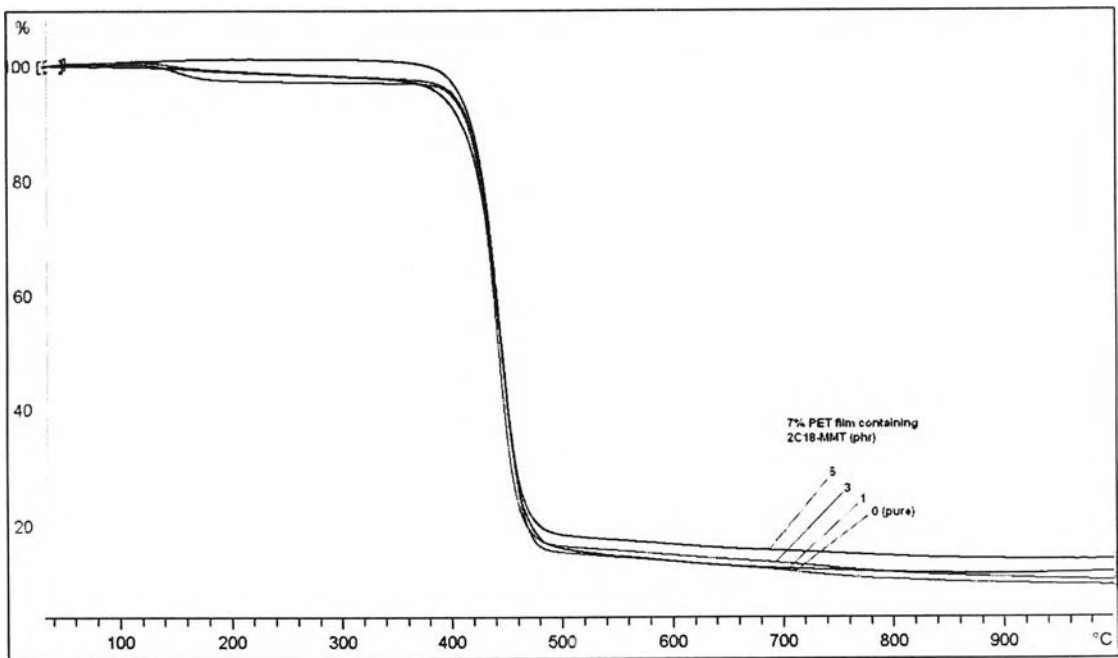
(a) unmodified-MMT
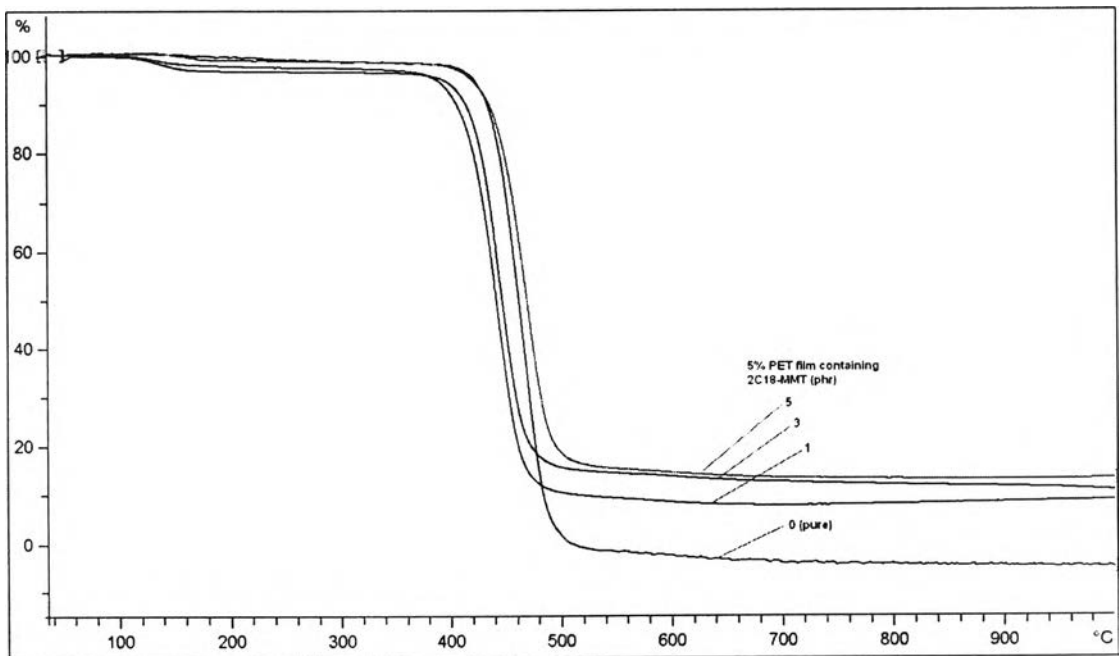
(b) organoclay

Figure 4.20 The effect of clay content on thermal properties at 5% PET nanocomposite film contained (a) unmodified-MMT and (b) organoclay
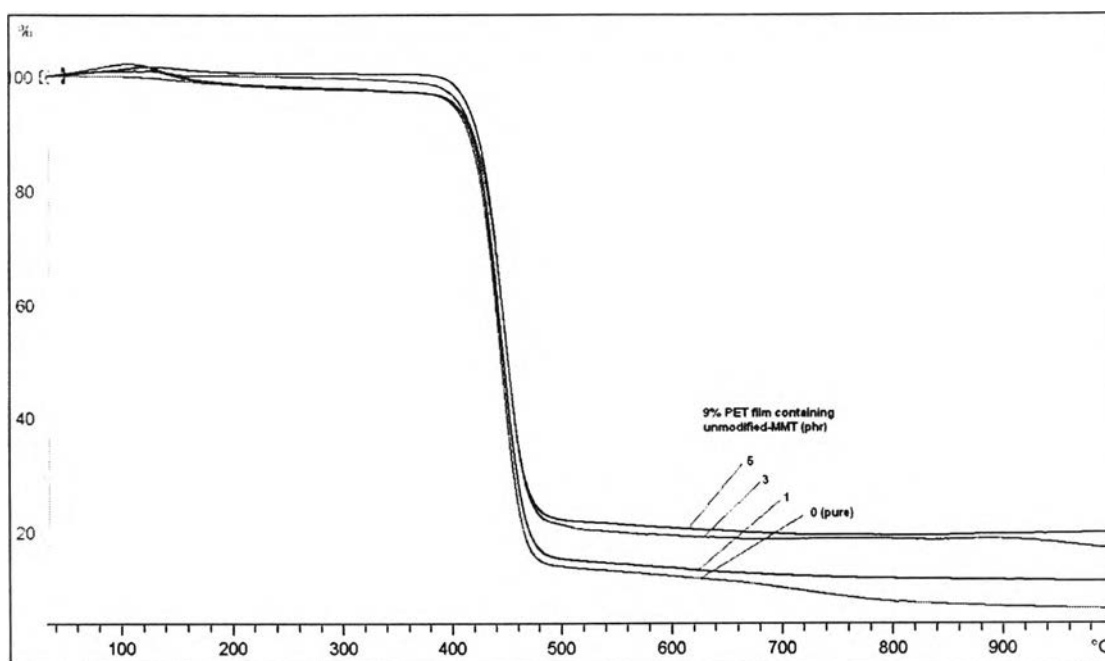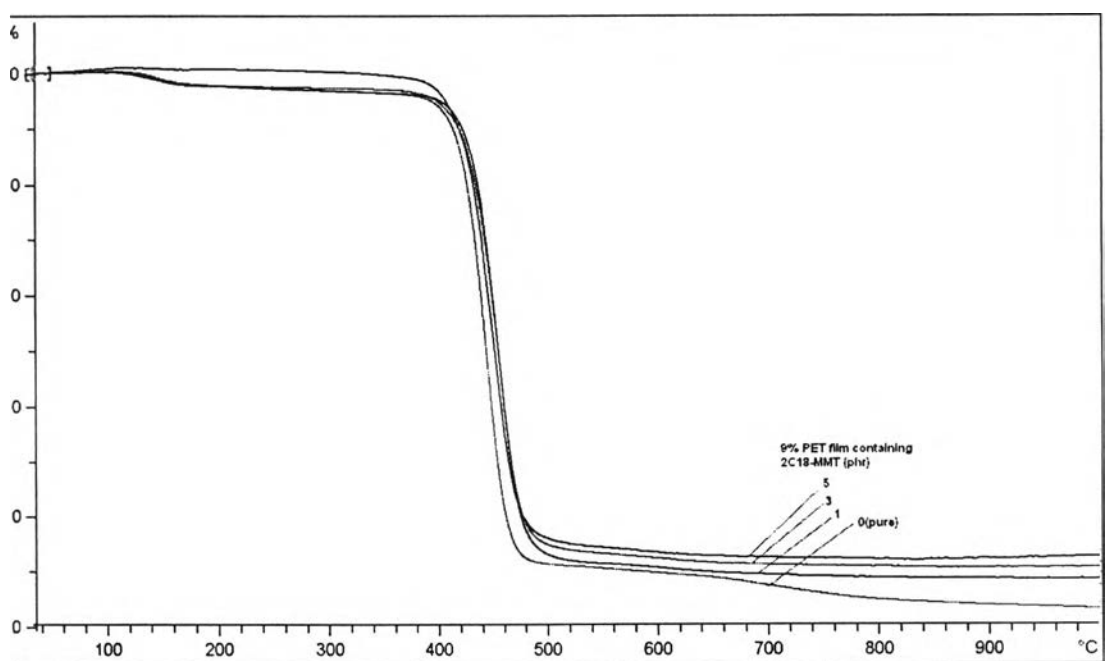
(a) unmodified-MMT

(b) organoclay

Figure 4.21 The effect of clay content on thermal properties at 7% PET nanocomposite film contained (a) unmodified-MMT and (b) organoclay

(a) unmodified-MMT

(b) organoclay

Figure 4.22 The effect of clay content on thermal properties at 9% PET nanocomposite film contained (a) unmodified-MMT and (b) organoclay

It can be concluded from the above results that although the initial degradation of nanocomposite film decreased if the clay content is greater than 1 phr,

the left char at 600 $^\circ$C increased due to the incorporation of the unmodified-MMT and organoclay. The increasing of the char formation is attributed to the high heat-resistance as well. These results are in good agreement with previously reported by other researches [9, 11, 22, 54-55]. From these results, the best thermal stability is 9% w/v PET nanocomposite films containing 1 phr of either type of clays.

4.3.2 Differential Scanning calorimetry

The obtained results of the thermal properties including melting point (T_m), enthalpy of fusion (ΔH_f), and degree of crystallinity are summarized in Table 4.6.

The effect of PET concentration on the thermal properties using DSC is shown in Figure 4.23 and Table 4.6. It can be seen that when increasing PET concentration, the melting temperature (T_m) slightly increases. For example, at 3% organoclay nanocomposite, the T_m of 5%, 7%, 9% PET is 247.58, 248.00, 249.06 $^\circ$C, respectively. It can be explained that when PET concentration increases, the number of polymer chain increases. So, the heat which was used to destroy all amount of polymer chain also increased. This result is similarly with the results from TGA analysis that $T_d^{'}$ increased with the PET concentration.

Figure 4.24 (a) and (b) depict second heating runs of 7% PET and its nanocomposite containing unmodified-MMT and organoclay, respectively. It is clear that there is an endothermic melting peak in all samples. The percent crystallinity is determined from the area of melting peaks which is converted into the heat of fusion (ΔH_f). Considering the effect of clay type, at 7% PET, it seems that there is no significant difference in the T_m between the organoclay and unmodified clay /PET nanocomposites.

From Figure 4.23 and 4.24, the interesting feature of the melting endothermic peak can be observed. The DSC thermograms of PET and its nanocomposite show two peaks of melting temperature. Generally, the multimelting behavior seems to be common to many thermotropic liquid crystalline polymer, and it is also observed for many conventional polymer such as poly (ethylene terephthalate) [56],

Table 4.6 The thermal properties of PET and its nanocomposite films

| PET (%w/v)	unmodified-MMT (phr)	organoclay (phr)	Melting (from heating scan)			Crystallization (from cooling scan)	
			T_m ($^{\circ}$C)	ΔH_f (J/g)	χ_c^{a}(%)	T_{Conset} ($^{\circ}$C)	T_c ($^{\circ}$C)
5	-	3	247.58	55.78	39.81	-	-
7	-	-	248.39	56.73	40.49	208.16	198.40
	1	-	248.94	60.92	43.48	206.44	198.04
	3	-	247.98	61.5	43.90	206.54	197.04
	5	-	247.86	53.84	38.43	206.80	200.50
	10	-	247.65	51.79	36.97	204.80	197.10
	-	1	248.21	71.4	50.96	209.60	204.22
	-	3	248.00	53.62	38.27	207.65	200.53
	-	5	248.21	53.6	38.26	207.14	200.11
	-	10	247.52	53.27	38.02	208.12	200.85
9	-	3	249.06	51.34	36.65	-	-

[a] degree of crystallinity
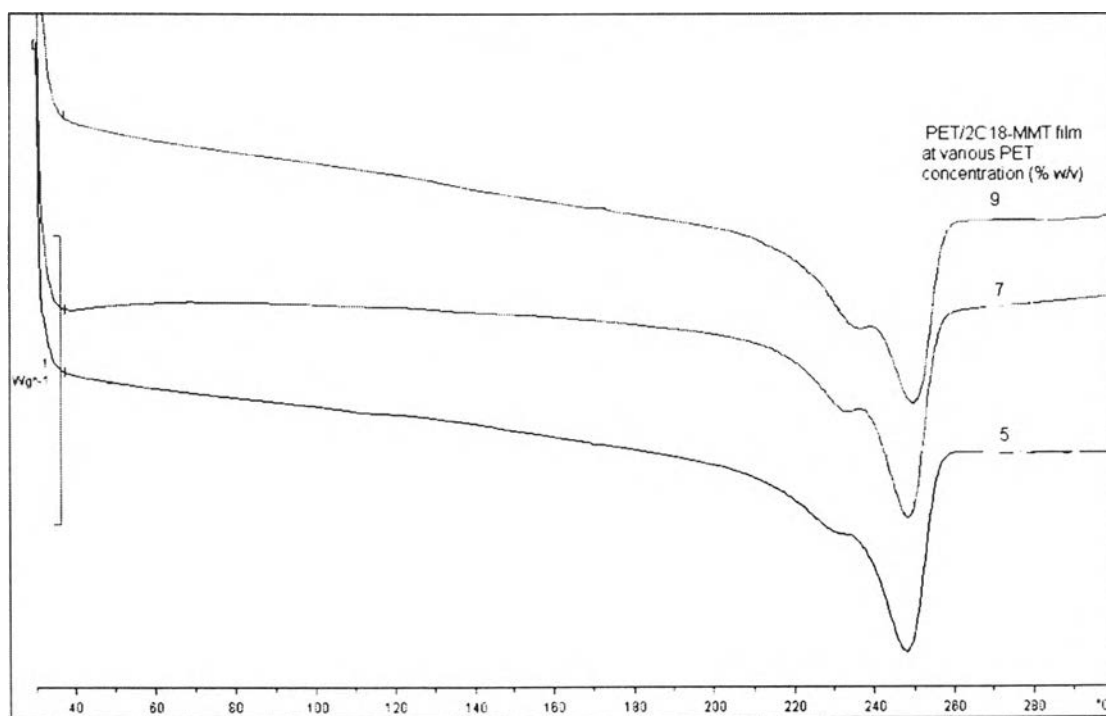
Figure 4.23 The DSC thermograms of various PET concentrations: 5%, 7%, and 9% at
3 phr 2C18-MMT

nylon 10, 12 [57]. This behavior can be resulted from many reasons, for example, varying from different crystal structure or lamellar thickness, to simultaneous melting and recrystallization. In this study the multimelting point may cause from the film processing resulting in the different crystal structure or less perfect crystals. The onset of melting temperature is related to the less stability of crystallites. A decrease (2-4 $^\circ$C) of the onset temperature of melting is found in the nanocomposite with respect to that of neat PET (247 $^\circ$C), as shown in appendix D.

Figure 4.26 shows the effect of clay on the degree of crystallinity of 7 % PET and its nanocomposite films. From this figure, it can be seen that compared to the pure PET film the degree of crystallinity of nanocomposite films containing 1 phr of both type of clay is greater. And comparing between two types of clay, the % crystallinity of organoclay /PET nanocomposite films (50.96%) is higher than that of unmodified clay nanocomposite films (43.48%). However, % crystallinity dramatically decreases when the clay content increases up to 5 phr. These results can be described that the dispersion of organoclay is better than the unmodified clay and a few of clay content also fully exfoliates. The clay platelets can act as the nucleating agent at lower content of clay [53]. The high surface area of silicate platelet has induced a nucleating effect. On the other hand, clay plays an effective nucleating agent in nylon1212/ MMT [58]. In this system, the high surface area of silicate platelet has induced a nucleation effect. Crystals may growth on the surface of the layer; therefore, the layers serve as seeds for spherulite growth. When increasing the clay content, the clay will be hard to disperse and tends to agglomerate. The larger size of clay can no longer act as the nucleating agent.

To confirm the effect of clay, especially organoclay, as a nucleating agent at lower amount of clay, Figure 4.26 presents the DSC thermograms from cooling scan of PET and its nanocomposite films. It is clearly seen that there is a distinct exothermic crystallization peak in all of cooling scans. The crystallization temperature (T_c) and the crystallization temperature (T_{Conset}) are listed in Table 4.6. From this table, it can be seen that the crystallization temperature (T_c) of organoclay/PET nanocomposite films is higher than that of pure PET film and unmodifiedclay/PET nanocomposite films.

Considering the amount of organoclay, the T_c values were found to shift to the higher temperature upon the addition of 1 phr of organoclay (204.22^o) and then decrease with increasing content of organoclay. However. all of the organoclay/PET nanocomposite films crystallized at a higher temperature region acted as nucleating agents for PET. In other words, the organoclay promoted the formation of heterogeneous nuclei and among them 1 phr of organoclay was the best in shifting the crystallization exotherm towards a higher temperature. These results also indicated that the crystallization of PET nanocomposite films contained 1 phr 2C18-MMT can be easily form crystals due to the nucleating effect as well.

Conclusively, in this study, the melting temperature show no significant difference with the clay content and the % crystallinity of PET/MMT nanocomposites containing 1 phr of both types of clay is grater than that of the neat PET films due to the smaller crystal size of PET and effective nucleating agent of clay.
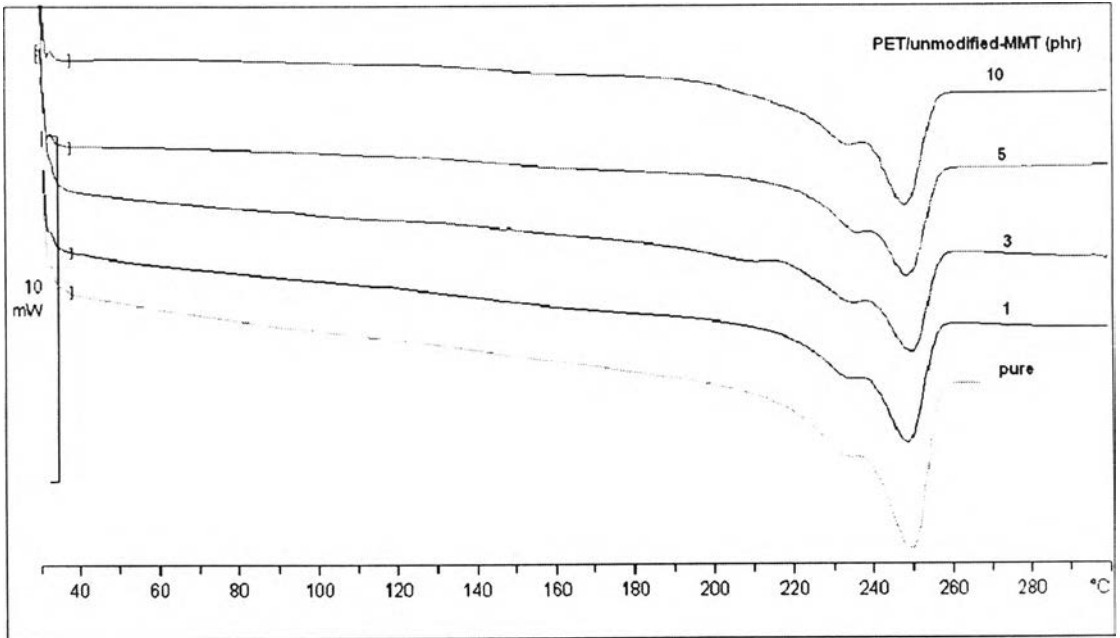
(a) unmodified-MMT
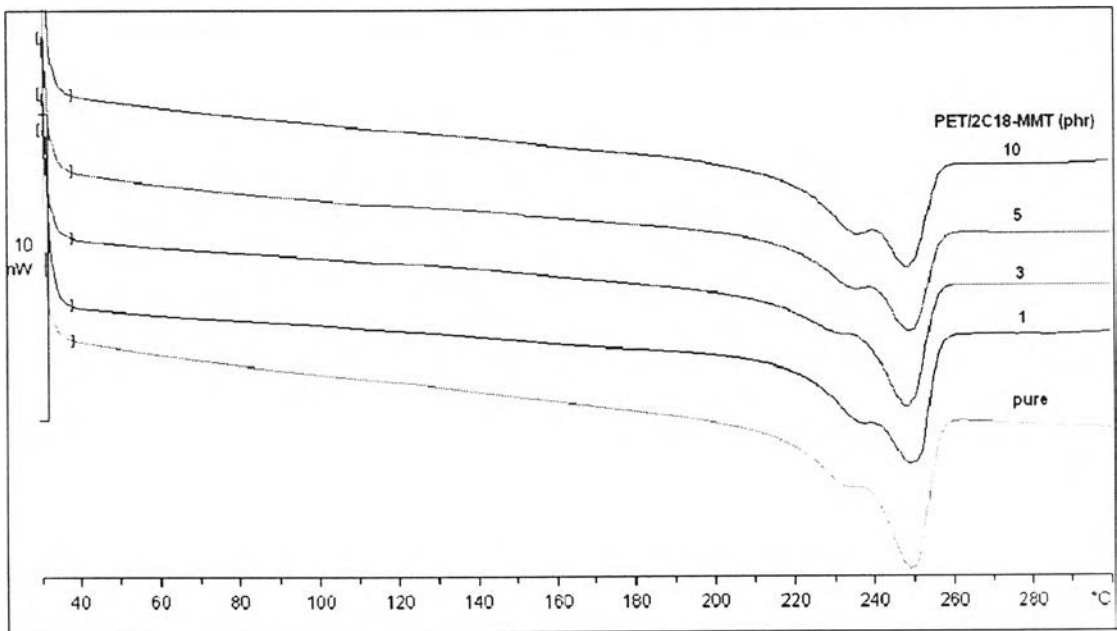
(b) organoclay

Figure 4.24 The DSC thermograms (from heating scan) of 7% PET and its nanocomposite films contained 1, 3 and 5 phr (a) unmodified-MMT and (b) organoclay
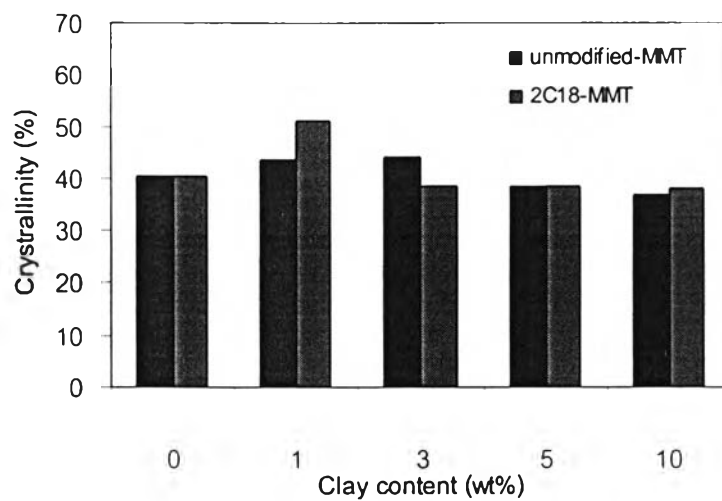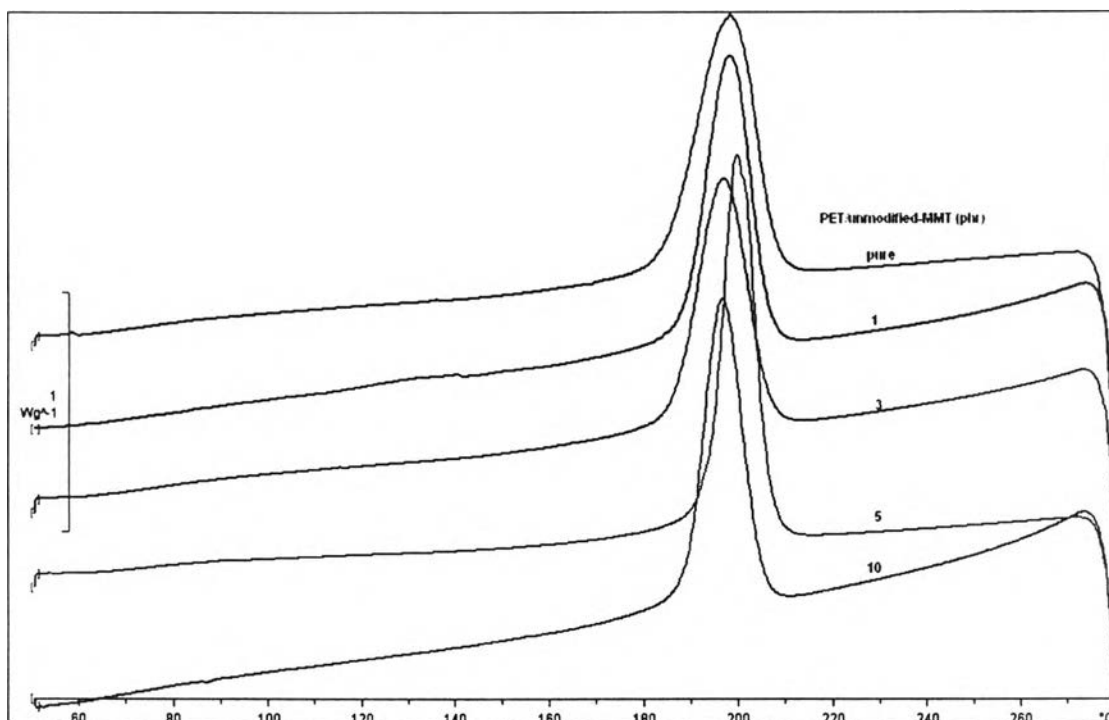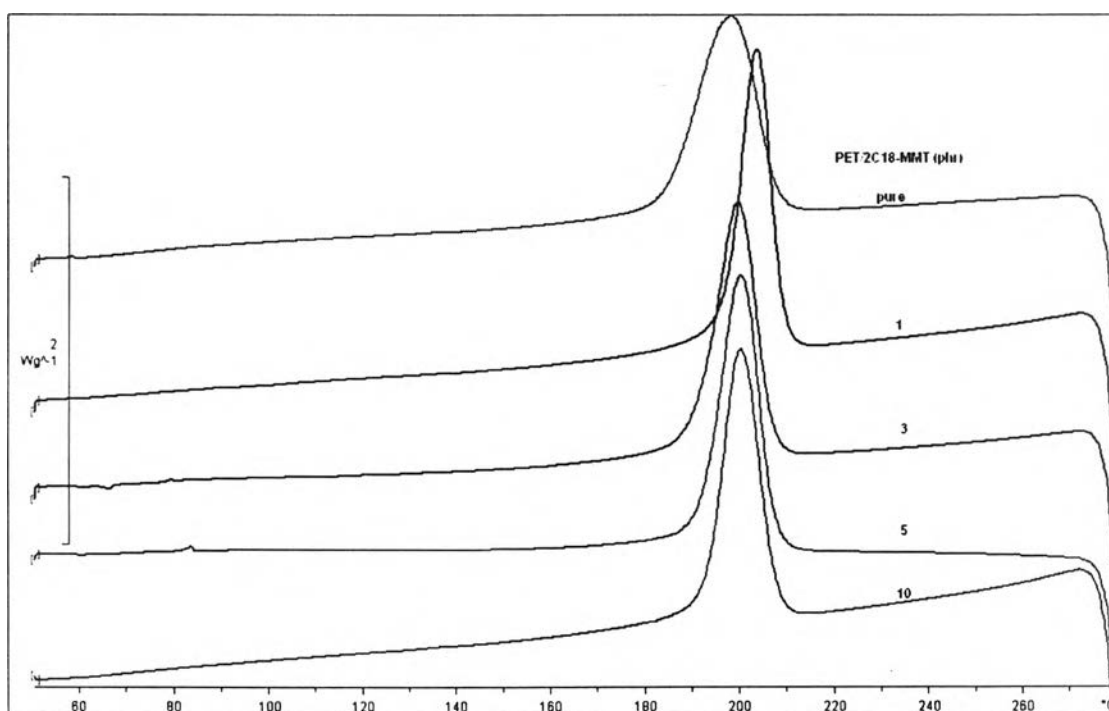
Figure 4.25 The effect of clay type and clay content on the % crystallinity of 7% PET and its nanocomposite films

(a) unmodified-MMT

(b) organoclay

Figure 4.26 The DSC thermograms (from cooling scan) of 7% PET and its nanocomposite films contained 1, 3 and 5 phr (a) unmodified-MMT and (b) organoclay