CHAPTER V

ACTIVE PACKAGING BASED ON ETHYLENE SCAVENGER PP/ORGANOMODIFIED BENTONITE NANOCOMPOSITES

5.1 Abstract

Na-bentonite was treated with quaternary alkyl ammonium ion, DOEM surfactant by ion exchange reaction in order to increase the d-spacing of the clay mineral. The organomodified bentonites were characterized by XRD, FTIR and TGA. Polypropylene was compounded with 3% wt organomodified bentonite by twin screw extruder using 6% Surlyn® as a reactive compatibilizer. Aluminium hydroxide and aluminium acetate were used as ethylene scavenger and were mechanically mixed with organomodified bentonite prior to compound with PP. The compounded pellets were fabricated into packaging film by using blow film extrusion. Dispersion of the organomodified bentonite and ethylene scavenger in the packaging film was observed by SEM. The ethylene gas permeability, thermal and mechanical properties of the nanocomposite active packaging films was investigated. The degradation temperature of the nanocomposites packaging film was improved. The addition of ethylene scavenger also affected the mechanical properties of the active packaging films.

5.2 Introduction

Active packaging contains active component allowing a controlled interaction between the food, package and internal gaseous environment, thus extends shelf life, improves fruit and vegetable safety or provides superior sensory quality. Active packaging techniques for preservation and improving quality and safety of food can be divided into three categories; absorbers (i.e. scavenger), releasing system and other systems. Absorbing (scavenging) systems remove undesired compounds such as oxygen, carbon dioxide, ethylene, excessive water, taints and other specific compounds [1].

The main problem of a prolonged shelf-life of fresh fruits and vegetables is ethylene gas. Ethylene absorbers system can use in the sachets form and packaging films [2]. Ethylene gas can form complex with Al [3] and adsorb on the surface of clay mineral [4]. In order to produce the polypropylene active packaging film based on clay mineral and aluminium compound, the clay mineral is treated with quaternary alkyl ammonium surfactant and the compatibilizer need to be induced in to the system.

The propose of this work is to prepare the active packaging based on the treated Na-bentonite by ion exchange reaction and aluminium compounds which are aluminium hydroxide and aluminium acetate by using Surlyn® as a rective compatibilizer. The thermal and mechanical properties of active packaging film were also investigated. The efficiency of the active packaging films was determined via ethylene gas permeability constant. The dispersion of organomodified bentonite and ethylene scavenger was observed by SEM.

5.3 Experimental

A. Materials

Na-bentonite (Mac-Gel® GRADE SAC) was supplied by Thai Nippon Co., Ltd. Thailand and DOEM surfactant (Stepantex VB 85) was supplied by Union Carbide Co., Ltd. Thailand. Ethanol 99.8% v/v was commercially purchased from Carlo Erba. PP under commercial name of Polene (1126 NK), MFI =11 was com-mercially purchased from IRPC Public Co., Ltd. Thailand. The compatibilizer, Sur-lyn® ionomer (PC 350) was supplied by DuPont (Thailand) Co. Ltd. Aluminium hydroxide (47% Al_2O_3), powder LR was purchased from Laboratory Rasayan Co., Ltd. Aluminium acetate, basic (powder) was purchased from Sigma Co., Ltd.

B. Preparation of organomodified bentonite with ethylene scavenger

In container, 350 g of Na-bentonite was swollen in 10 L of water for 24 hr, and in another container DOEM as an alkyl ammonium ion (1.5CEC) was dissolved in 1600 ml of water/ethanol (1/1, v/v) solution. Then, the solution was heated at 80 °C until it became transparent. Then solutions of two containers were vigorously mixed for 2 hr at 80 °C 1000 rpm and homogenized at 600 rpm for 30 min. The organo-modified bentonite was filtered and washed with hot water several times. It was dried in a vacuum oven at 100 °C overnight and ground into 325 mesh under [5].

The ethylene scavenger chemicals are aluminium trihydroxide (ATH) and aluminium acetate (AlAc). Aluminium hydroxide 5, 10, and 15% wt of 3%wt organomodified bentonite in the nanocomposite were mixed with the organomodified bentonite by mechanical mixing.

C. Ethylene Scavenger PP/ Organomodified bentonite Nanocomposites

Polypropylene was blended with 6%wt of Surlyn® ionomer by using a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm. The operating temperatures of extruder were maintained at 80, 170, 180, 190, 200, and 210°C from hopper to die, respectively. The screw speed was 50 rpm. The obtained pellets were dried under vacuum at 80^0C. Polypropylene with compatibilizer was dry-mixed with 3% wt of organo-modified bentonite and 5, 10, and 15%wt of aluminium compounds by shaking them in an internal-mixer for 10 min. Then , they were melt mixing by twin screw extruder, a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm. The operating temperatures of extruder were maintained at 80, 170, 180, 190, 200, and 210°C from hopper to die, respectively. The screw speed was 50 rpm. After drying, the composite pellets were fabricated into the packaging film by tubular blown film extrusion. The screw speed was 50 rpm, screw diameter was 45 mm, L/D was 26 and the processing temperature were 210 °C from hopper to die.

The thermal stability of the nanocomposite films were determine by burning the samples from 30-800 °C in a Perkin-Elmer Pyris Diamond TG/DTA Analyzer. The crystallization and melting behaviors of the ethylene scavenger PP/organo-modified bentonite nanocomposite films were measured with a Perkin-Elmer DSC 7 analyzer. During the crystallization experiment, the specimens were first melted at 250°C, and then cooled to room temperature at 10°C/min rate. The specimens were subsequently heated at 10°C/min for the corresponding melting behavior investigations.

The crystal structures of ethylene scavenger PP/organo-modified bentonite nanocomposites were also analyzed by Wide angle X-ray diffraction (WAXD) using a Rigaku Model Dmax 2002 performed in the 2θ of 2-50 degrees with the scan speed 2θ/min.

The dispersion of organo-modified bentonite and aluminium compounds in the nanocomposite films was observed by SEM (JEOL/JEM 5800 LV)

The aluminium contents in the ethylene scavenger nanocomposite films were determined by EDX mode of SEM and AAS. The nanocomposite films were heat at

450 °C for 1 hr. The residual was digested by hydrofluoric acid (HF) to prepare the sample solution then analyzed by using Varian, StectrAA 300.

Tensile tests were performed at room temperature according to ASTM D882 using a Lloyd Universal Testing Machine. The specimen dimension is 10x150 mm. Yield strength and strain at break were measured using an extensometer at a cross-head speed of 50 mm/min, load cell 500 N. The data reported from seven specimens were averaged to determine mechanical properties.

Ethylene gas permeability was measured according to ASTM D1434 by using GDP/E Brugger Munchen. Determine the slope of the graph, N by dividing the time (s) by the scale division (mm). The gas permeability rate, G in units of $cm^3/(m^2.day.bar)$ is calculated from

$$G = \frac{77.76x10^{10}\, xV}{78.5Kx29N}$$

where V = volume of the evacuation chamber = 0.4370 cm^3

K = absolute temperature (degrees Kelvin) = 300 K

Ethylene gas permeability, P in units of ml (STP)/m^2.d.atm is calculated from

$$P = G \times T \times 5.164 \times 7.725$$

where T = thickness of polymer films (mm) = 0.03 mm

5.4 Results and Discussion

A. Thermal behavior of ethylene scavenger PP/organobentontie nanocomposite film

The melting and crystallization behavior, as measured by DSC, of PP and ethylene scavenger PP/organomodified bentonite nanocomposite films are shown in Figure 5.1 and Table 5.1. DSC scanning was carried out in the temperature range between 30-250 °C corresponding to the melting point of PP (160-170 °C). When compared to PP, the ethylene scavenger PP/organomodified bentonite nanocopomsite films have lower % crystallinity, melting temperature and crystallization temperature. These are the results from the disturbance of organomodified bentonite and ethylene scavenger during crystalline formation process [6].

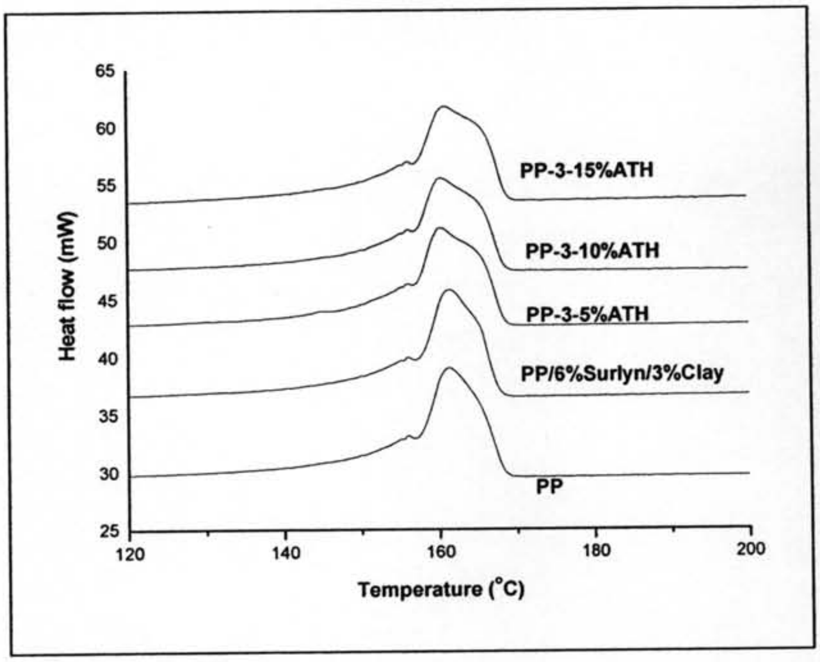
Table 5.1 Melting and crystallization behavior of PP and ethylene scavenger PP/organomodified bentonite nanocomposite films

Films	T_m (°C)		T_c (°C)		ΔH_m	Crystallinity
	Onset	Peak	Onset	Peak	(J/g)	(%)
PP	157.68	163.03	121.28	116.13	88.85	42.51
PP/6%Surlyn/3%Clay	157.61	162.37	119.38	114.63	81.35	35.42
[1]PP-3-5%ATH	156:07	161.03	117.10	111.63	85.00	37.01
PP-3-10%ATH	156.01	160.37	116.37	111.80	85.45	37.21
PP-3-15%ATH	156.08	160.37	115.33	111.63	85.43	37.20
[2]PP-3-5%AlAc	155.48	160.87	115.29	110.63	85.13	37.07
PP-3-10%AlAc	154.90	161.53	117.10	110.63	102.48	37.73
PP-3-15%AlAc	155.88	160.37	115.91	111.30	87.69	38.18

PP 100% Crystallinity, ΔH_m = 209 J/g

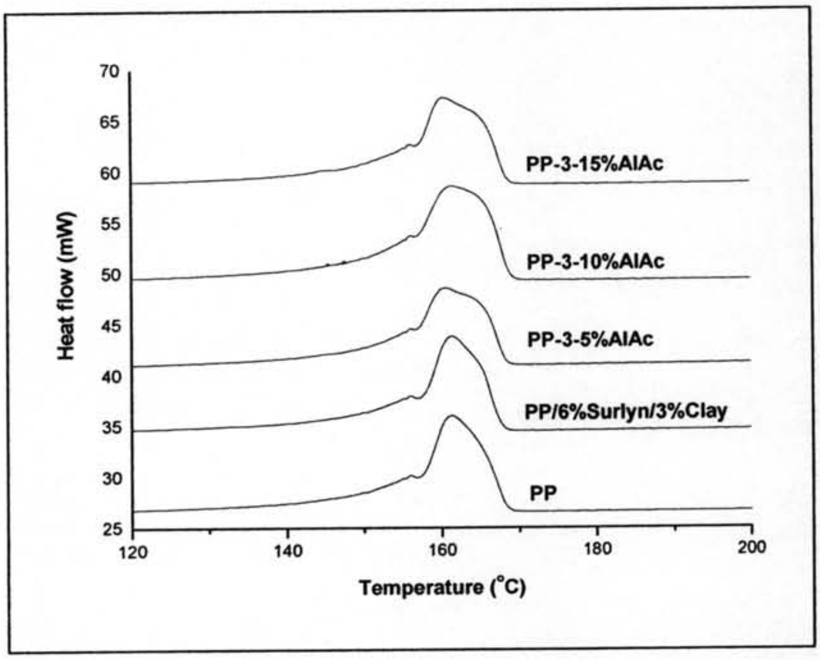
[1]PP-3-x %ATH = Blended PP/6%Surlyn/3%Clay with x %wt of aluminium hydroxide by 3% wt of organomodified bentonite

[2]PP-3-x %AlAc = Blended PP/6%Surlyn/3%Clay with x %wt of aluminium acetate by 3% wt of organomodified bentonite



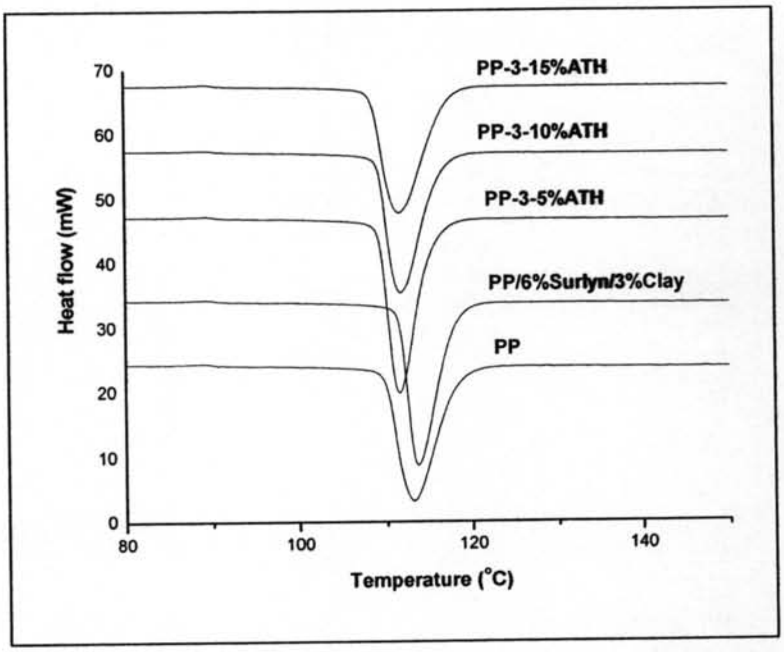
Heat flow (mW)
65
60
55
50
45
40
35
30
25
120
140
160
180
200
Temperature (°C)
PP-3-15%ATH
PP-3-10%ATH
PP-3-5%ATH
PP/6%Surlyn/3%Clay
PP

(a-1)



Heat flow (mW)
70
65
60
55
50
45
40
35
30
25
120
140
160
180
200
Temperature (°C)
PP-3-15%AlAc
PP-3-10%AlAc
PP-3-5%AlAc
PP/6%Surlyn/3%Clay
PP

(a-2)



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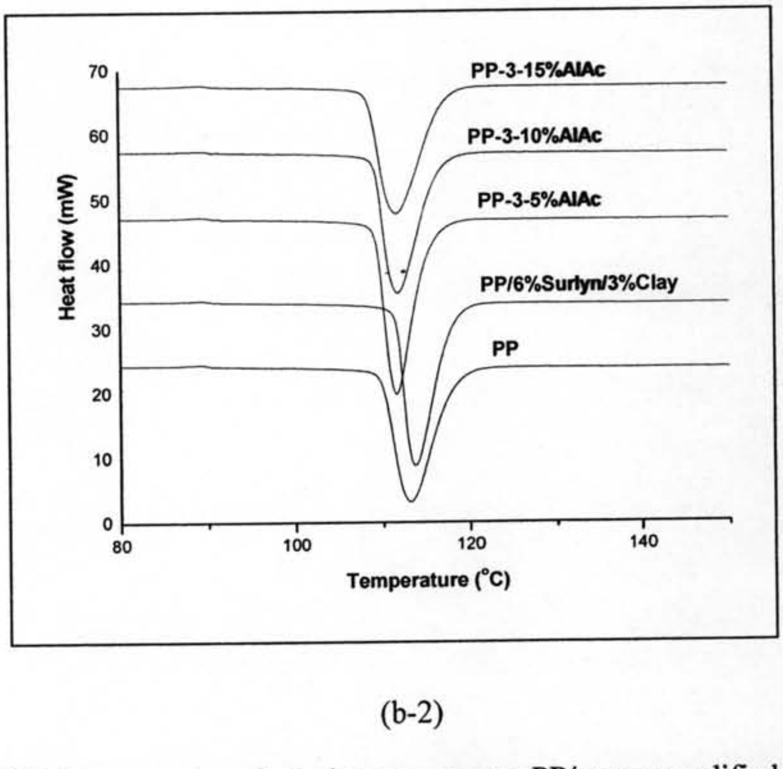


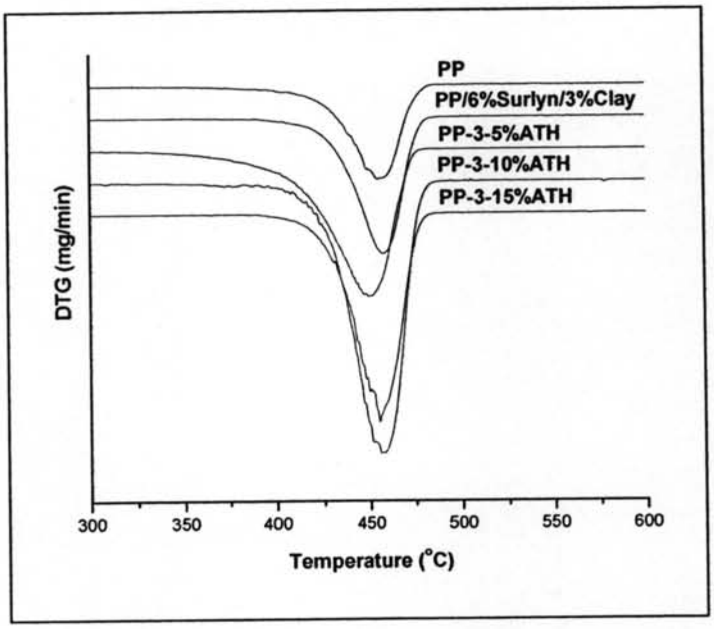
(b-2)

Figure 5.1 DSC thermograms of ethylene scavenger PP/organomodified bentonite nanocomposites film (a-1) Melting Temperature of ATH system,(a-2) Melting Temperature of AlAc system, (b-1) Crystallization Temperature of ATH system and (b-2) Crystallization Temperature of ATH system.

Summary of TGA experimental results for the nanocomposite films is shown in Table 5.2 and Figure 5.2 and 5.3. The residual contents are the component of clay mineral and aluminium compounds. The incorporation of organomodified bentonite and aluminium compounds into PP improved the degradation temperature. The presence of metal oxides in organomodified bentonite such as silica, aluminium and magnesium was attributed to this improvement [7].

Table 5.2 Thermal behavior of PP and ethylene scavenger PP/organomodified bentonite nanocomposite films

Sample	**TGA**			
	Residual Content (wt %)	**T_d (°C)**	**T_i (°C)**	**T_f (°C)**
PP	-	454.50	432.80	487.40
PP/Surlyn/3%Clay	1.20	459.90	439.00	487.90
PP-3-5%ATH	5.20	449.80	419.00	463.20
PP-3-10%ATH	3.40	457.60	433.30	468.60
PP-3-15%ATH	6.60	454.90	436.20	466.80
PP-3-5%AlAc	1.30	453.80	433.80	468.20
PP-3-10%AlAc	2.50	455.90	431.80	467.10
PP-3-15%AlAc	4.80	455.00	430.50	466.40



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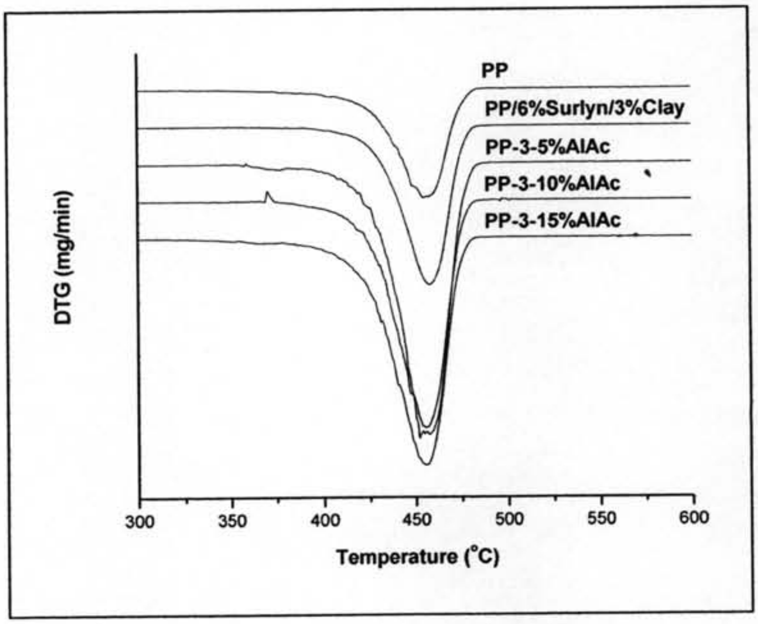

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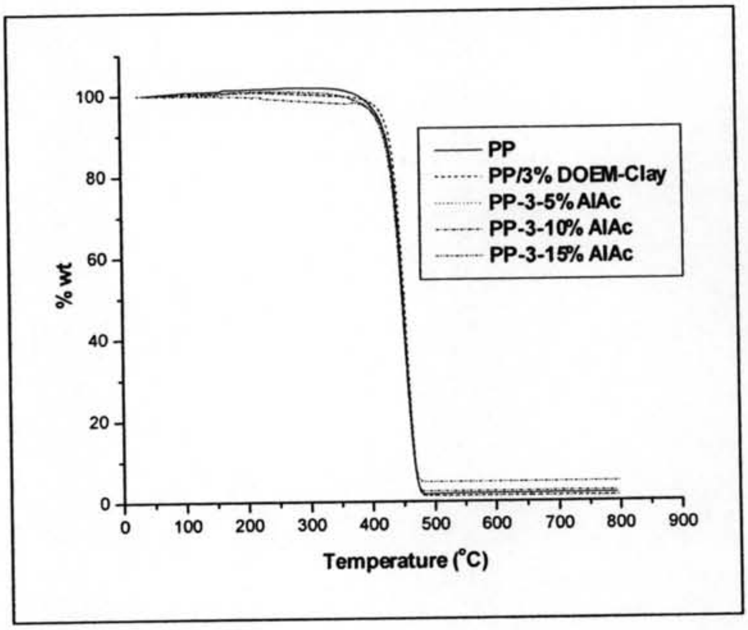
Figure 5.2 DTA curves of ethylene scavenger PP/organomodified bentonite nano-composite films (a) ATH system and (b) AlAc system.



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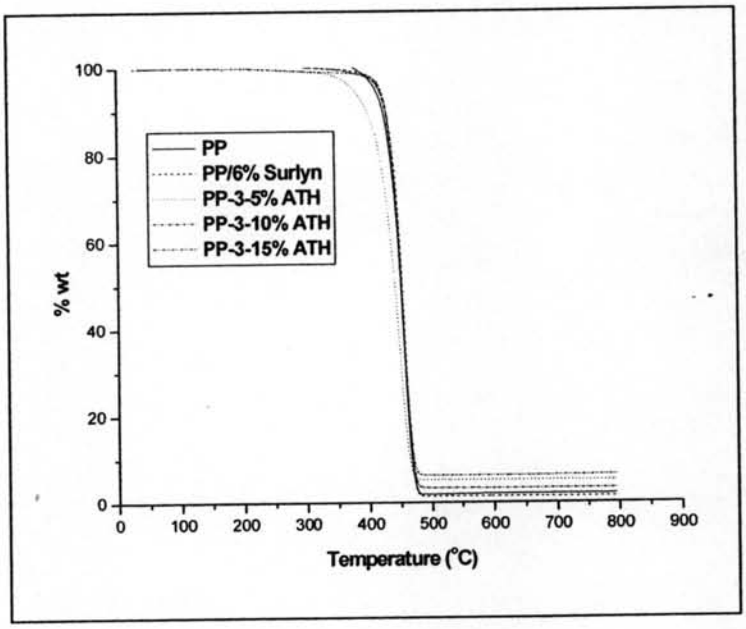


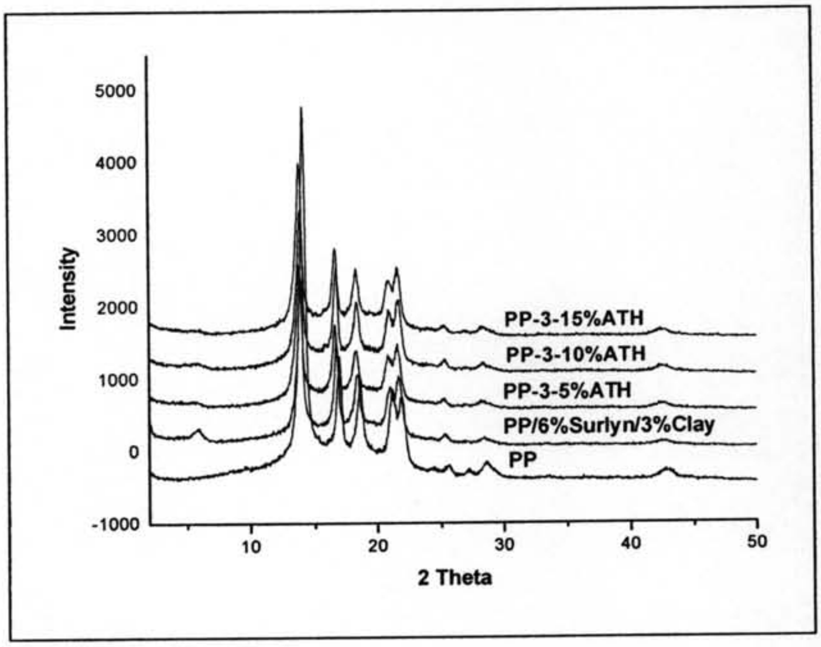
(b)

Figure 5.3 TG curves of ethylene scavenger PP/organomodified bentonite nano-composite films (a) ATH system and (b) AlAc system.

B. Crystallization behavior of ethylene scavenger PP/organomodified bentonite nanocomposite films

The structure of the nanocomposites was examined by XRD. The characteristic peaks of PP crystal peak were analyzed within the 2θ range of 2-50°, as shown in Figure. 5.4. The results showed that the incorporation of organomodified bentonite and aluminium compounds does not affect the crystal structure of PP [8].

The XRD patterns of PP and ethylene scavenger PP/organomodified bentonite nanocomposites 2θ = 2-10° in Figure 5.5 shows that nearly exfoliations are occurred in the nanocomposite films due to the absence of the peak (001) that corresponding to the reflections of the clay mineral [9].



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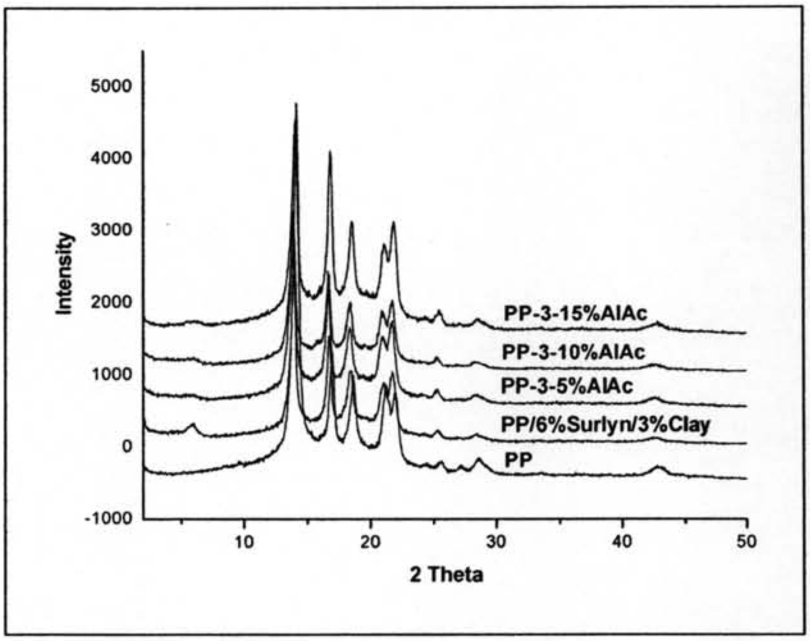

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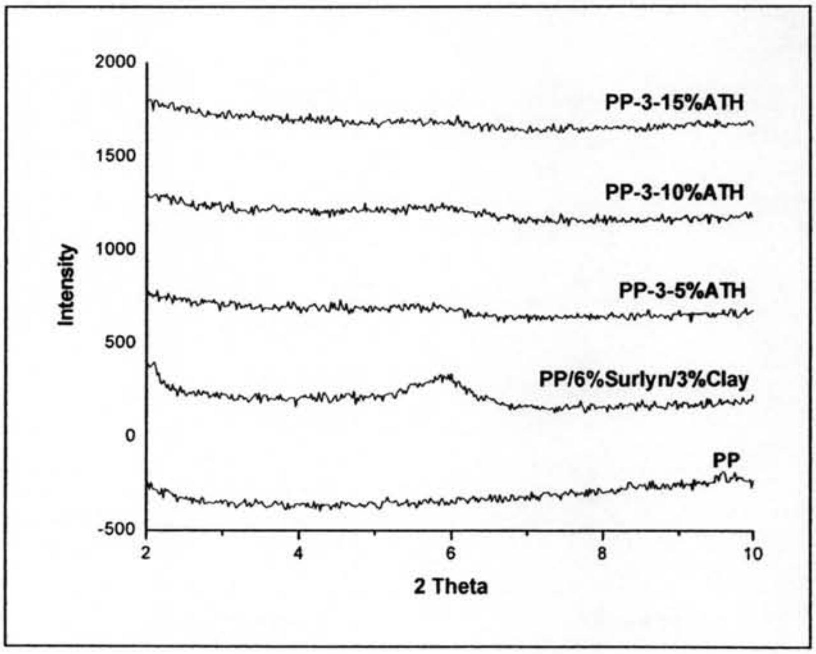
Figure 5.4 The XRD patterns of PP and ethylene scavenger PP/organomodified bentonite nanocomposites $2\theta = 2\text{-}50^\circ$ (a) ATH system and (b) AlAc system.



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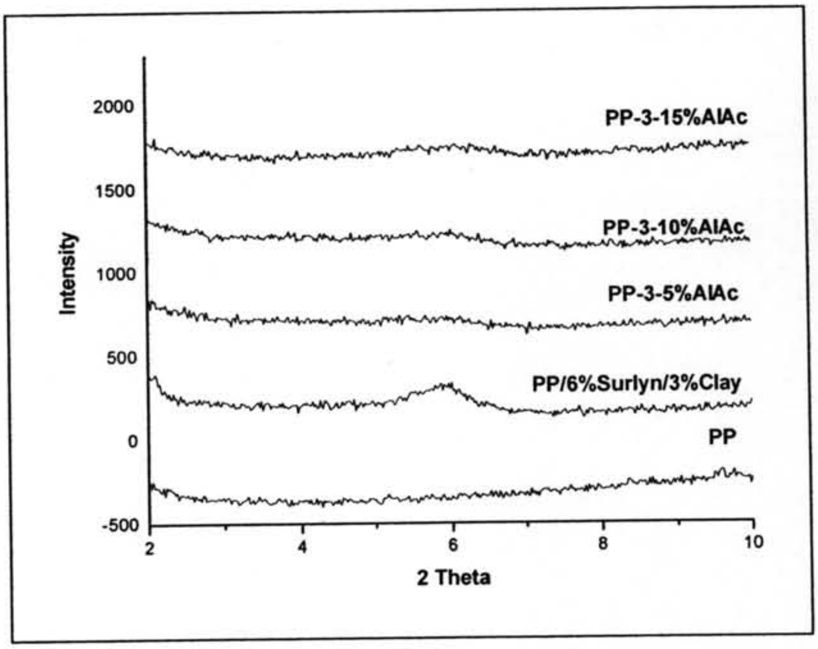


(b)

Figure 5.5 The XRD patterns of PP and ethylene scavenger PP/organomodified bentonite nanocomposites $2\theta = 2\text{-}10^{\circ}$ (a) ATH system and (b) AlAc system.

C. Mechanical properties of ethylene scavenger PP/organomodified bentonite nanocomposite films

Figure 5.6 shows that the Young's modulus of the active packaging films decrease when compared with PP and PP/organomodified bentonite but when increasing content of the aluminium compounds Young's modulus increased. This implies that the stress is transferred from polymer to inorgannic filler [10].

Figure 5.7 shows the effect of organomodified bentonite and aluminium compound loading on tensile strength of PP films. The tensile strength is reduced when add the aluminium compounds into the system. The agglomeration of the organomodified bentonite and aluminium compounds act as a stress concentration point and effect the polymer film easy to break [11].

The effect of organomodified bentonite and aluminium compound on elongation at break is shown in Figure 5.8. Adding organomodified bentonite and aluminium compounds into PP matrix slightly decreases the elongation at break due to the ogranobentonite and aluminium compounds obstructing the movement of PP along the applied force [12].

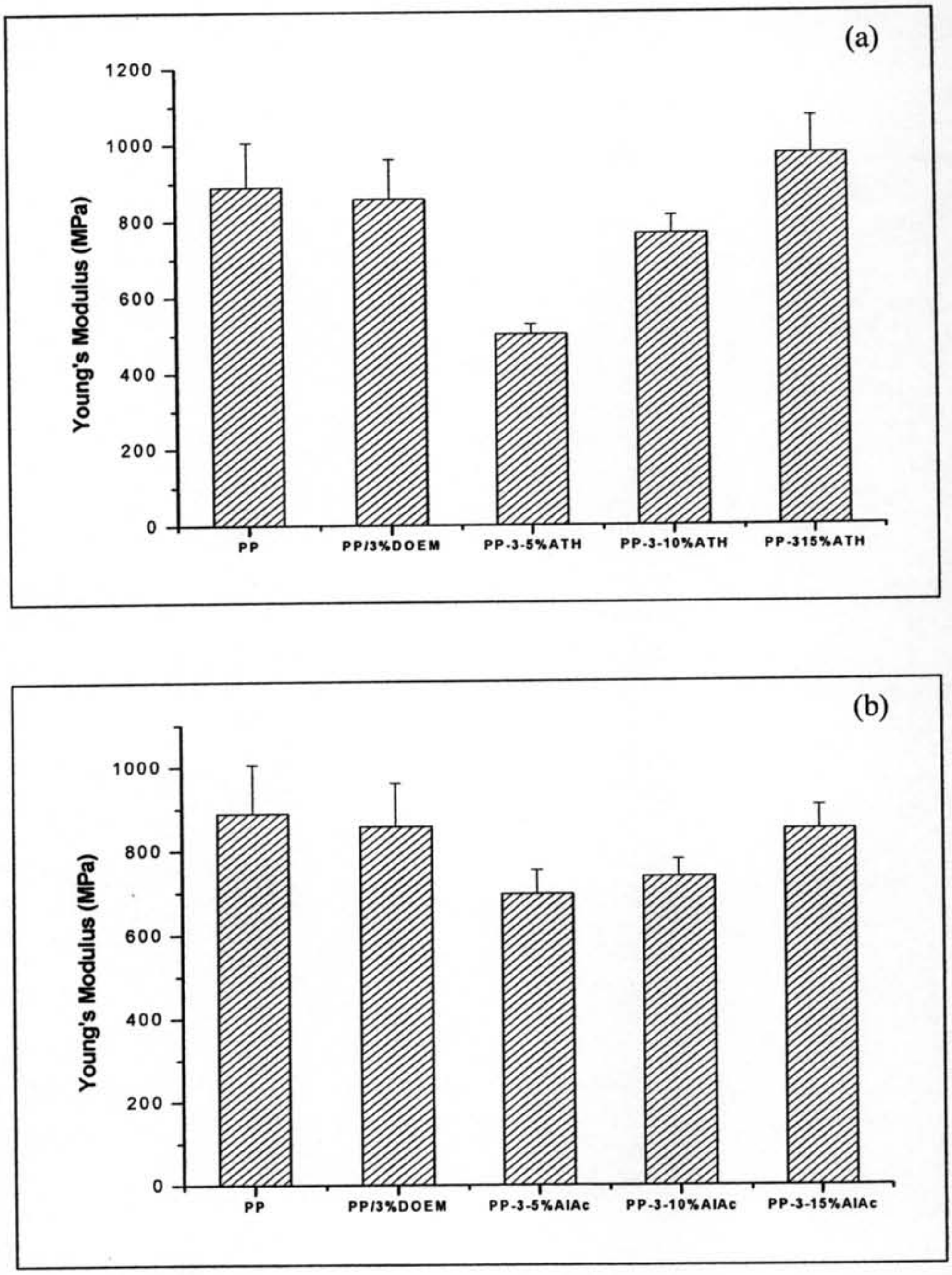
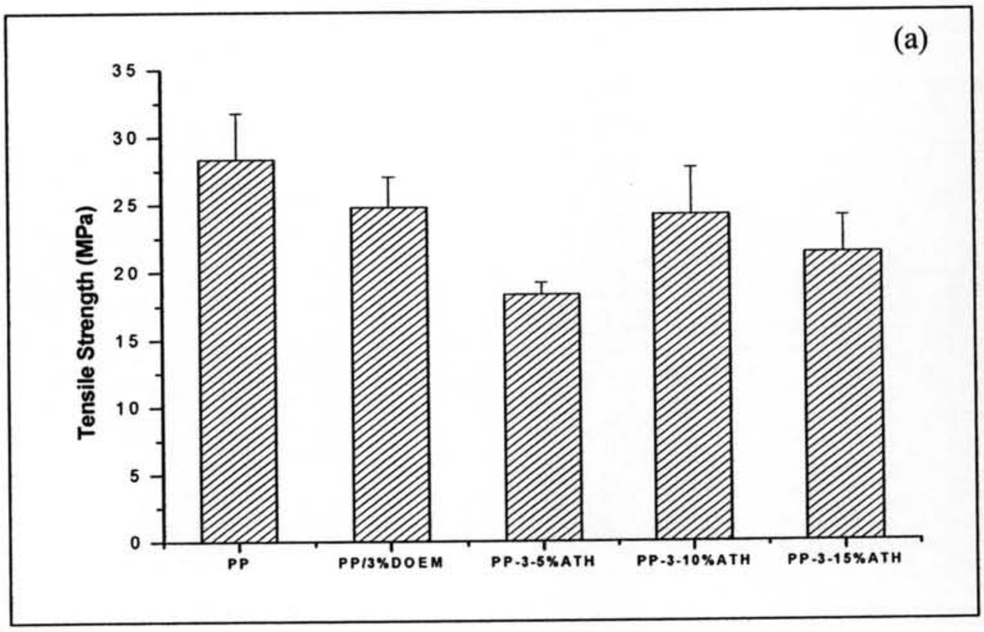


Figure 5.6 Young's modulus of PP and ethylene scavenger PP/organomodified bentonite nanocomposite films (a) ATH system and (b) AlAc system.



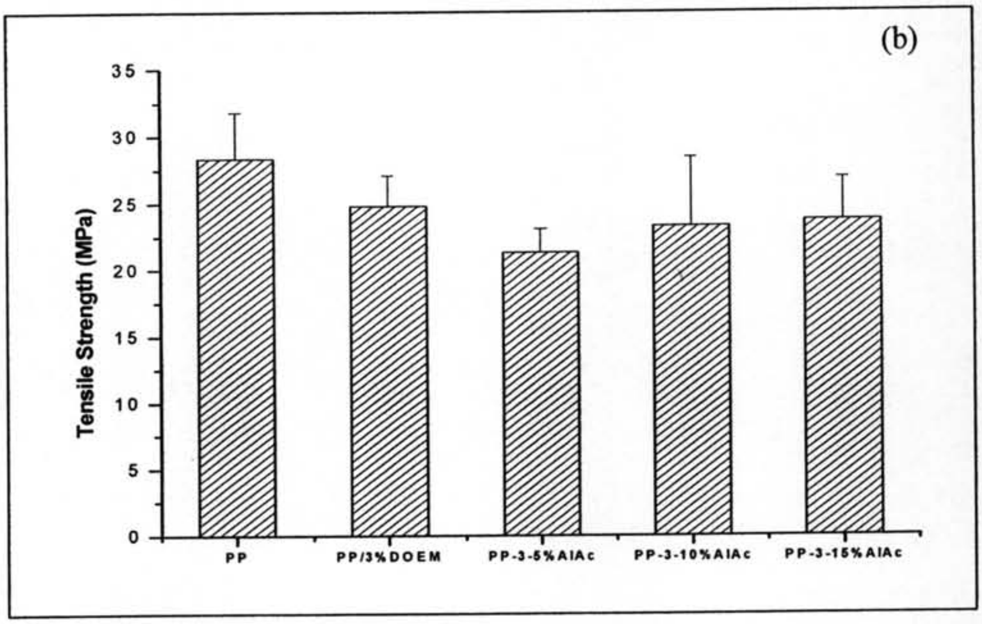


Figure 5.7 Tensile strength of PP and ethylene scavenger PP/organomodified bentonite nanocomposite films (a) ATH system and (b) AlAc system.

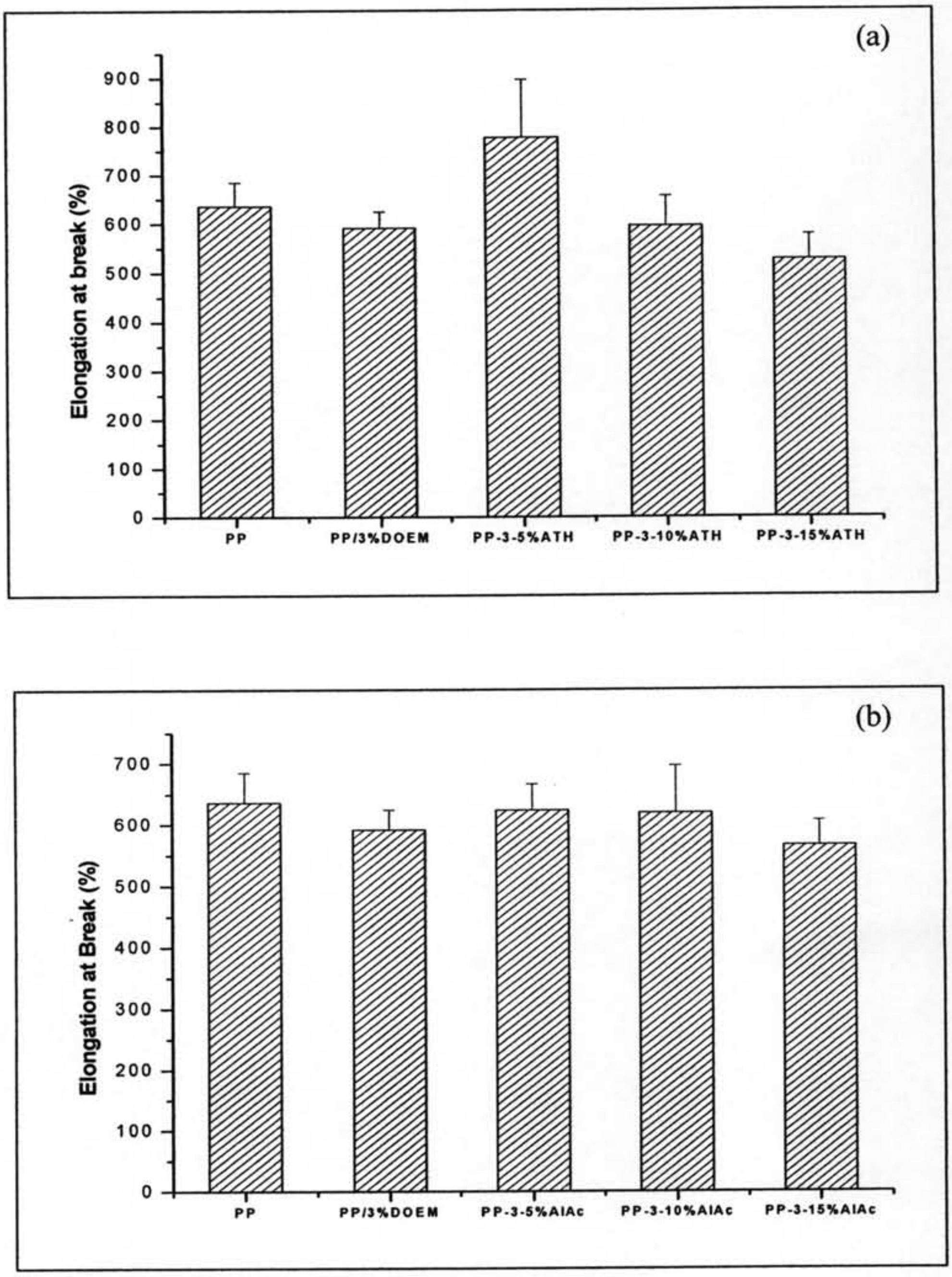


Figure 5.8 Elongation at break (%) of PP and ethylene scavenger PP/organomodified bentonite nanocomposite films (a) ATH system and (b) AlAc system.

D. Dispersion of ethylene scavenger and organomodified bentonite in nanocomposites films

The content of element on the active packaging film shows in Table 5.3 and 5.4. When increasing the content of aluminium compound the amount of Al and O increase. The dispersion of organoclay and aluminium compound shown in Figure 5.9, aluninium hydyoxide system showed better dispersion in PP film than aluminium acetate. When increasing content of aluminium compounds the agglomeration occured as the small nodules in the nanocomposite films[13].

Table 5.3 Percent element on surface of ethylene scavenger PP/organomodified bentonite nanocomposite films by EDX

Sample	% Element			
	C	O	Al	Si
PP/Surlyn/3%Clay	93.53	5.63	0.11	0.73
PP-3-5%ATH	91.84	7.36	0.13	0.66
PP-3-10%ATH	91.59	7.38	0.21	0.82
PP-3-15%ATH	92.19	6.82	0.24	0.75
PP-3-5%AlAc	91.07	7.94	0.14	0.85
PP-3-10%AlAc	91.55	7.37	0.17	0.91
PP-3-15%AlAc	91.78	7.31	0.19	0.72

Table 5.4 Percent Al in ethylene scavenger PP/organo-modified bentonite nano-composite films by AAS

Sample	**Al (ppm)**	**Al (%wt)**
PP/Surlyn/3%Clay	14.5	6.73
PP-3-5%ATH	14.4	6.65
PP-3-10%ATH	22.6	10.75
PP-3-15%ATH	28.8	12.97
PP-3-5%AlAc	15.7	7.53
PP-3-10%AlAc	15.9	7.66
PP-3-15%AlAc	20.4	9.82

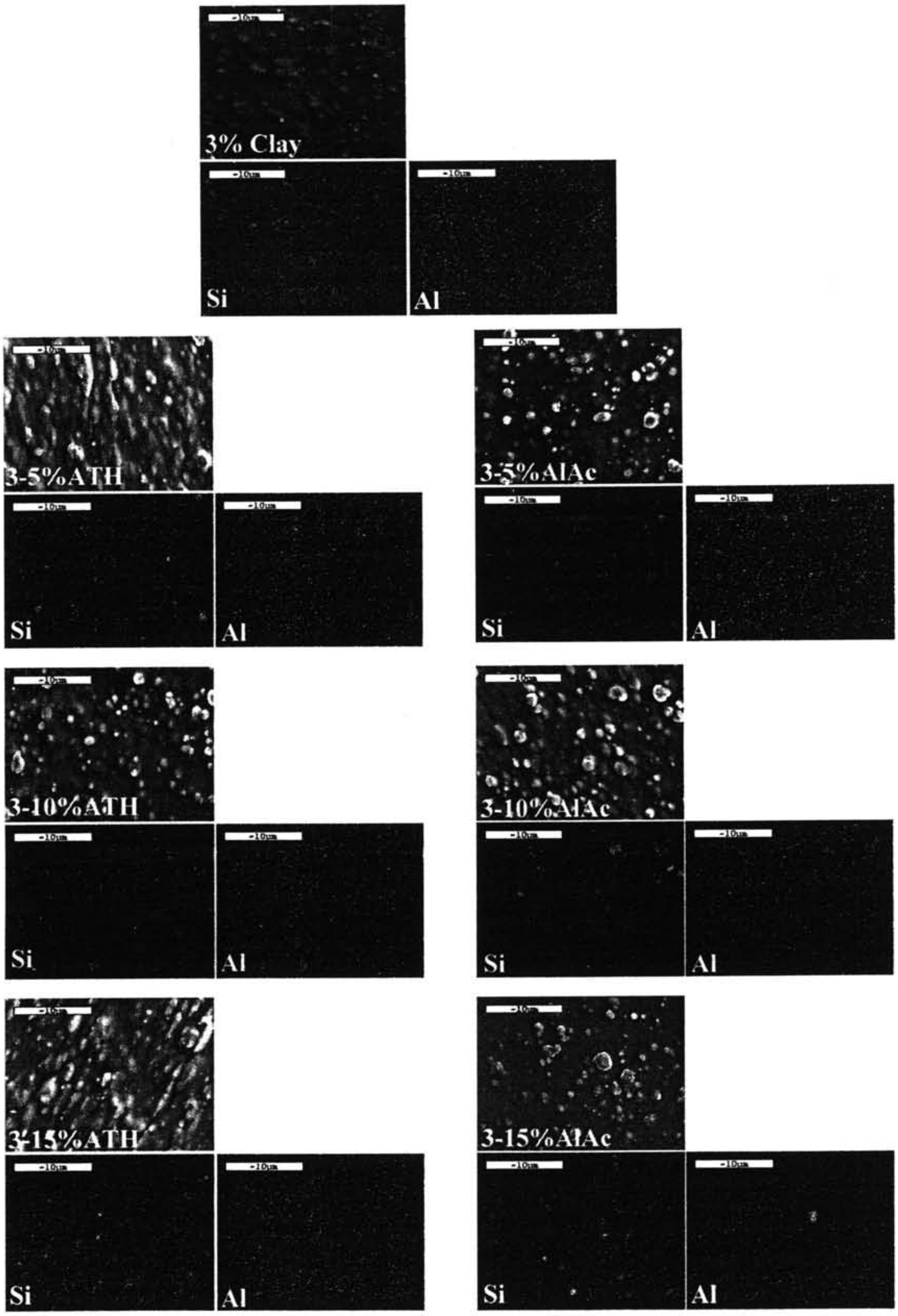
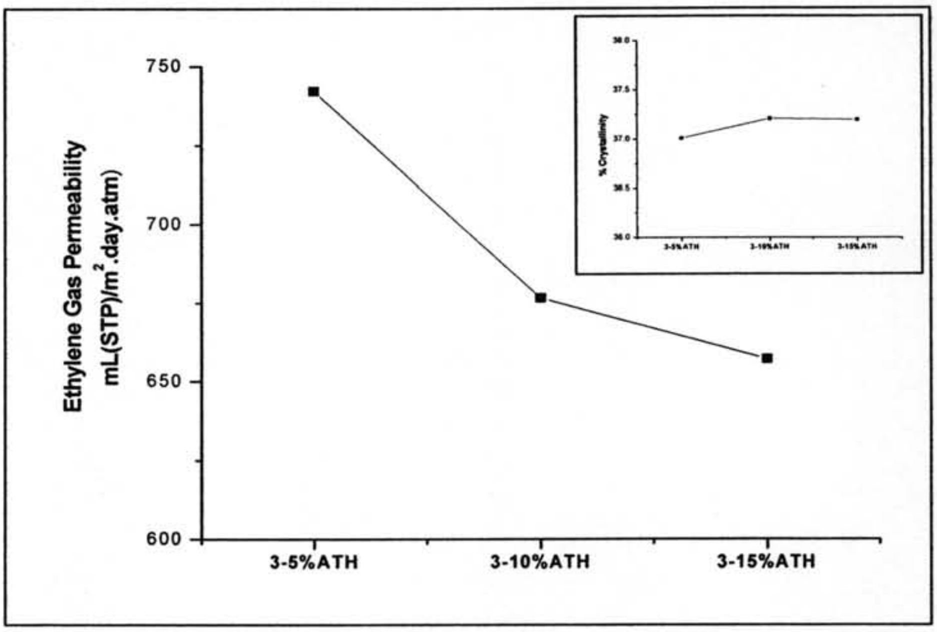


Figure 5.9 SEM images and Al and Si mapping of ethylene scavenger PP/organo-modified bentonite nanocomposite films.

E. Ethylene gas permeability of ethylene scavenger PP/organomodified bentonite nanocomposite films

The ethylene gas permeability of ethylene scavenger PP/organomodified bentonite nanocomposites films shows in Figure 5.10. The ethylene gas permeability of PP/6%Surlyn/3%Clay is 568.75 ml (STP) m^2.day.atm and % crystallinity is 35.42. This reveals that aluminium compounds may introduce some micro void due to poor compatibility with PP and thus raising higher permeability; however, due to its acidity, ethylene gas is better absorbed and thus lowering the ethylene permeability with increasing aluminium compounds content [14]. The crystallinity of ethylene scavenger PP/organomodified bentonite nanocomposites films is in the same range so that it shows small effect to the ethylene gas permeability.



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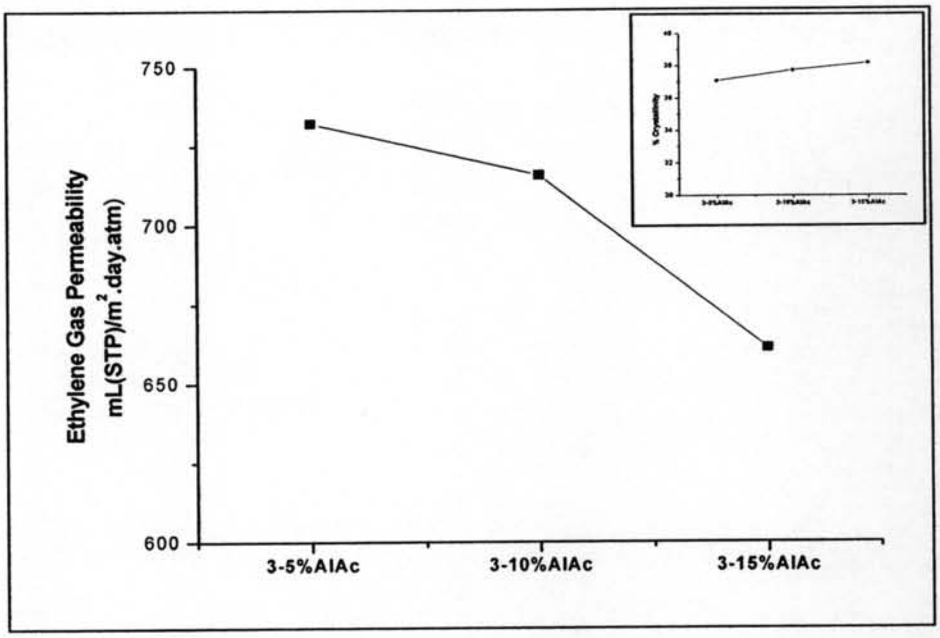

(b)

Figure 5.10 Ethylene gas permeability constant of ethylene scavenger PP/organomodified bentonite nanocomposite films (a) ATH system and (b) AlAc system.

5.5 Conclusions

Aluminium compounds which are aluminium hydroxide and aluminium acetate are used as ethylene scavengers. The aluminium compounds were mixed as 5, 10 and 15 % wt of 3% organomodified bentonite of nanocomposites to prepare ethylene scavenger active packaging films. The addition of aluminium compound into PP reduced % crystallinity, melting temperature and crystallization temperature of PP. These are the result from the disturbance of organomodified bentonite and ethylene scavenger during crystalline formation process. However the crystal structure of PP was not affected by the existence of organomodified bentonite. Young's modulus, tensile strength and elongation at break of the active packaging films were reduced when compare with PP. When increase the content of aluminium compounds Young's modulus and tensile strength increased but elongation at break reduced. These due to the agglomeration of organomodified bentonite and aluminium compoumds. The ethylene permeability decreases when increasing the content of aluminium compounds.

5.6 Acknowledgements

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