



CHAPTER V

ACTIVE PACKAGING BASED ON ETHYLENE SCAVENGER PP/ORGANOMODIFIED BENTONITE NANOCOMPOSITES

5.1 Abstract

Na-bentonite was treated with surfactant, StepantexTM SP-90, by ion exchange reaction in order to increase the d-spacing of the clay mineral and obtain organomodified-BTN. The organomodified-BTN was characterized by XRD, FTIR and TGA. Then, it was also treated with 3-aminopropyltrimethoxysilane and incorporated with polypropylene, aluminum hydroxide/ calcium hydroxide in twin screw extruder using 6% Surlyn[®] as a reactive compatibilizer. Aluminium hydroxide and calcium hydroxide were used as ethylene scavenger and carbon dioxide scavenger, respectively. The compounded pellets were fabricated into packaging films using blow film extrusion process. The dispersion of the organomodified bentonite and ethylene scavenger within the packaging film was observed by SEM. Moreover, the ethylene gas permeability, thermal and mechanical properties of the nanocomposite active packaging films were 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

Due to fruits and vegetables are perishable products with active metabolism during the post harvest, therefore, packaging plays an important role in maximizing the shelf life of them. However, traditional-packaging concepts are limited in their ability, thus, the new food packaging has been introduced to control the interaction between package and internal gaseous environment. Therefore, the variety of active packaging technologies have been developed in order to extend shelf life while the packaged food maintain safety and quality as well. Important active packaging systems include carbon dioxide emitter/absorbers, moisture absorbers, ethylene absorbers, ethanol emitters, flavor releasing/absorbing systems, time-temperature indicators, and antimicrobial containing films.

The main problems of fresh fruits and vegetables are both ethylene and carbon dioxide gas. Ethylene (C_2H_4) is a growth-simulating hormone. It accelerates softening, ripening, and senescence by increasing the respiration rate, thereby decreasing shelf life. Hence, ethylene gas is removed from the package headspace to slow senescence and prolong shelf life. For carbon dioxide (CO_2) gas, it is formed due to deterioration and respiration reactions. The produced CO_2 should be removed from the package to avoid food deterioration and gas pressure built up inside rigid packaging or volume expansion in flexible packaging.

The purpose of this work is also to prepare ethylene and carbon dioxide scavenger film based on PP/modified clay. Clay minerals, Bentonite, were treated for exfoliated the clay platelets by surfactant (Stepantex-90). The ethylene and carbon dioxide scavengers are aluminum hydroxide and calcium hydroxide, respectively. The ethylene scavenger was attached to nanoclay by using 3-aminopropyltrimethoxysilane to act as surface treatment to stabilize the exfoliated state of organoclay, and then, compound with polypropylene to be nanocomposite pellets. However, carbon dioxide scavenger is incorporated with polypropylene by melt intercalation. Both of them are fabricated to be active packaging films. In addition, X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), and Thermogravimetric Analysis (TGA), was used for characterize this film. Mechanical properties, permeability, ethylene and carbon dioxide adsorption, and thermal properties of the obtained films were also investigated.

5.3 Experimental

A. Materials

Commercial sodium activated bentonite Mac-Gel[®] (GRADE SAC), Na-BTN, with cationic exchange capacitor (CEC) of 44.5 meq/100 g clay, was supplied by Thai Nippon Co., Ltd. Thailand. For the surfactant, dipalmitoylethyl hydroxyethyl monium methosulfate (Stepantex[™] SP-90), was received from Sunny World Co., Ltd. Moreover, ethanol 99.8% v/v was purchased from Carlo Erba and 3-aminopropyltrimethoxysilane was purchased from ACS Xenon Limited Partnership with trade name Fluka. The ethylene scavenger, aluminum hydroxide ($47\%Al_2OH_3$), was purchased from LabScan Asia Co., Ltd and calcium hydroxide ($Ca(OH)_2$), which is carbon dioxide scavenger, was purchased from ACS Xenon Limited Partnership

under trade name Fluka. Furthermore, polypropylene (Polene 1126 NK, MFI =11) was commercially purchased from IRPC Public Co., Ltd. Thailand. The compatibilizer, Sodium-neutralized ethylene-co-methacrylic acid (Surlyn® PC350, 4.5 MFI), was supplied by DuPont (Thailand) Co. Ltd.

B. Preparation of organomodified- BTN with ethylene/carbon dioxide scavenger

350g of Na-bentonite was swollen in 10L water for 24 hours. Alkyl ammonium ion (DOEM) is dissolved in 1600ml solution of water/ethanol (1v/v) at 80°C for 30 min. The swollen clay and alkyl ammonium ion solution are mixed together at 80°C for 2 hr with vigorously stirring, and follow by homogenized for 30 min. Then, the mixture is filtrated and washed with hot water several times. After that, it is dried in a vacuum oven overnight at 100°C and ground into powder through a sieve, 325 mesh [1]. After that, this powder is refluxed with 3-aminopropyl trimethoxysilane in solution of ethanol and water (75:25) at 70°C for 24hrs. The organoclay is purified by washing several times to eliminate the physisorbed silane and than dried in the oven. The ethylene scavenger is aluminium hydroxide, and carbondioxide scavenger is calcium hydroxide. It were mixed with the organomodified bentonite by mechanical mixing.

C. Ethylene or carbon dioxide scavenger PP/ organomodified-BTN Nanocomposites Films

The master batches containing 50 wt% organomodified clays with compatibilizer, Surlyn®, were firstly prepared. Then, the various contents of organomodified clays (1, 3 and 5 %wt), was compounded with PP and aluminium hydroxide/calcium hydroxide in twin screw extruder 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 performed at 80, 170, 180, 190, 200, and 210°C from hopper to die, respectively, with 50 rpm of screw speed. After that, these nanocomposites pellets were dried under vacuum at 80°C and fabricated into the packaging film by tubular blown film extrusion process. 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 nanocomposites films were obtained using a Perkin-Elmer Pyris Diamond TG/DTA Analyzer. The crystallization and melting

behavior of PP that incorporate with organoclay were investigated by Perkin-Elmer DSC 7 analyzer. The heat flow and temperature of the instrument were calibrated by indium which is a standard material. Nitrogen was purged within the equipment to prevent the thermal degradation. In addition, the specimens were first melted at 200°C, then, cooled down to room temperature at 10°C/min rate and they were also heated at 10°C/min for the corresponding melting behavior investigations.

The crystal structure of nanocomposites films were performed with XRD of a Rigaku Model Dmax 2002 performed at 2θ range of 2-40 degrees with scan speed 2 degree/min and scan step 0.01 degree.

The dispersion of organomodified-BTN in PP/organobentonite nanocomposite films were observed by SEM (JEOL/JEM 5800 LV)

The tensile tests were followed the ASTM D882 with Lloyd universal testing machine. Modulus is measured by extensometer at a crosshead speed 50 mm/min and load cell 500 N. The specimens are cut into rectangular shape with 10x100 mm and the experiments are taken under room temperature without preconditioning of the samples.

The oxygen gas permeability was measured according to ASTM D1434 by Oxygen Permeation Analyser Model 8000, Illinois Instrument Inc.

5.4 Results and Discussion

A. Thermal behavior of ethylene/carbon dioxide scavenger PP/organomodified-BTN nanocomposite films

From DSC results, the melting and crystallization behavior of PP and ethylene or carbon dioxide scavenger PP/organomodified bentonite nanocomposite films are shown in Figure 5.1 and Table 5.1. They were performed in the temperature between 30-200°C, which is corresponded to the melting point of PP (160-170°C). When compared to PP, the ethylene scavenger PP/organomodified-BTN nanocomposite films have higher % crystallinity, melting temperature and crystallization temperature. These are the results from the organomodified bentonite that acts as nucleating agent for crystallization of PP matrix [2].

Table 5.1 Melting and crystallization behavior of PP and ethylene/carbon dioxide PP/organoclay nanocomposite films

Samples	T _m (°C)	T _c (°C)	ΔH _m (J/g)	Crystallinity (%)
PP	158.37	108.63	69.46	33.74
PP/1%Clay/0.023Al	159.70	111.80	80.44	38.88
PP/1%Clay/0.046Al	158.53	112.13	76.68	37.05
PP/3%Clay/0.069Al	158.37	112.17	75.26	37.12
PP/3%Clay/0.138Al	158.67	112.63	71.08	37.03
PP/5%Clay/0.115Al	159.53	112.80	76.54	38.54
PP/5%Clay/0.230Al	159.87	113.80	74.24	37.39
PP/3%Clay/0.069Ca	159.37	111.80	76.44	37.71
PP/3%Clay/0.138Ca	159.53	111.97	76.67	37.81

PP 100% Crystallinity, ΔH_m = 209 J/g

Moreover, TGA results of the nanocomposite films are shown in Table 5.2 and Figure 5.2. The incorporation of organomodified bentonite and aluminum hydroxide/calcium hydroxide into PP is slightly improved the degradation temperature of nanocomposites films. The residual contents consist of the component of clay mineral and aluminum compounds. The presence of metal oxides in organomodified bentonite such as silica, aluminium and magnesium was attributed to this improvement [3].

Table 5.2 Thermal behavior of PP and PP/organoclay nanocomposites film

Sample	TGA			
	Residual Content (wt %)	T _d (°C)	T _i (°C)	T _r (°C)
PP	-	443.7	420.5	453.7
PP/1%Clay/0.023Al	4.2	444.1	428.8	454.9
PP/1%Clay/0.046Al	2.6	443.9	428.6	455.0
PP/3%Clay/0.069Al	0.5	444.4	429.9	454.9
PP/3%Clay/0.138Al	4.7	444.8	428.7	455.7
PP/5%Clay/0.115Al	2.6	445.6	429.1	455.9
PP/5%Clay/0.230Al	4.5	445.6	428.6	455.7
PP/3%Clay/0.069Ca	0.9	443.6	428.3	455.4
PP/3%Clay/0.138Ca	2.3	441.2	428.6	455.4

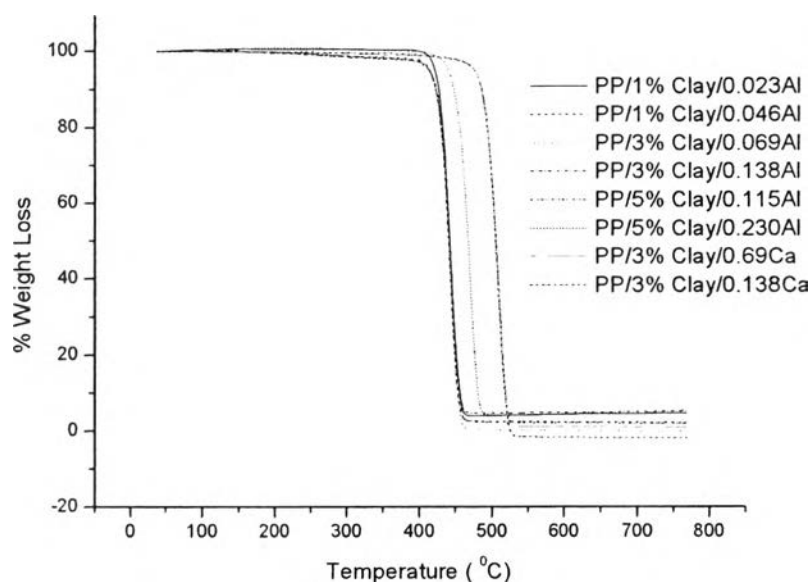


Figure 5.1 TG curves of ethylene/carbon dioxide scavenger PP/organomodified bentonite nanocomposite films

B. Crystallization behavior of ethylene/carbon dioxide scavenger PP/organomodified-BTN nanocomposite films

The crystallization of the nanocomposites films was examined by XRD. The characteristic peaks of PP crystal peak were analyzed within the 2θ range between 2–40 degrees, as shown in Figure. 5.4. As far as no peak or very small peaks were observed at 2–40° in the XRD pattern of exfoliated polymer nanocomposites due to loss of the structural registry of the layers. The absence of peaks in the nanocomposites either because of the clay has been completely exfoliated or delaminated with a much too large spacing between layers, or because the nanocomposites does not present ordering anymore [4, 5, 6].

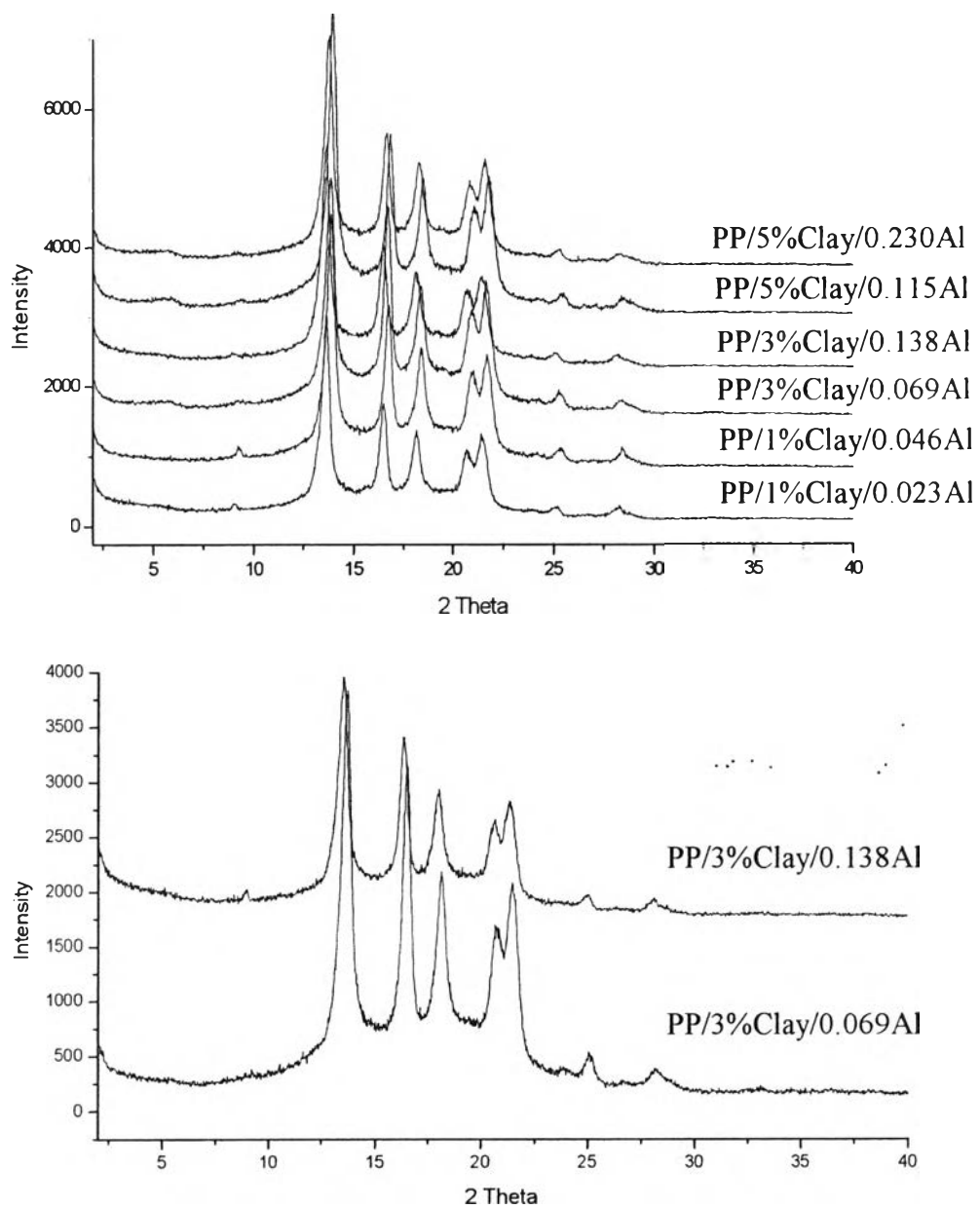


Figure 5.2 The XRD patterns of PP and ethylene/carbon dioxide scavenger PP/organomodified bentonite nanocomposites with $2\theta = 2-40^\circ$

C. Mechanical properties of ethylene/carbon dioxide scavenger PP/organomodified-BTN nanocomposite films

Figure 5.3 is the graph of Young's modulus of the active packaging films. When compared between PP and scavenger PP/organomodified bentonite nanocomposite films, these films were slightly increased at 1% organoclay. This implies that the stress is transferred from polymer to inorganic filler. However, Young's modulus was drop down at 3% and 5 wt %. Because, the aggregation of aluminum hydroxide, calcium hydroxide, or organoclay inside the films [6, 7].

Moreover, figure 5.4 shows the effect of organomodified bentonite and aluminium hydroxide/calcium hydroxide loading on stress at break of PP films. The stress at break is reduced when add the aluminum/calcium hydroxide and organoclay into the system. The incorporation of them into the PP matrix reduced the ability of the composites to transfer applied stress especially particulate filler with irregular shape, and the agglomeration of the organomodified bentonite and aluminium compounds act as a stress concentration point and effect the polymer film easy to break [8].

The effect of organomodified bentonite and aluminium/calcium compound on elongation at break is shown in Figure 5.5. Adding organomodified bentonite and aluminium/calcium hydroxide into PP matrix slightly decreases the elongation at break due to the organobentonite and aluminium compounds obstructing the movement of PP along the applied force [9].

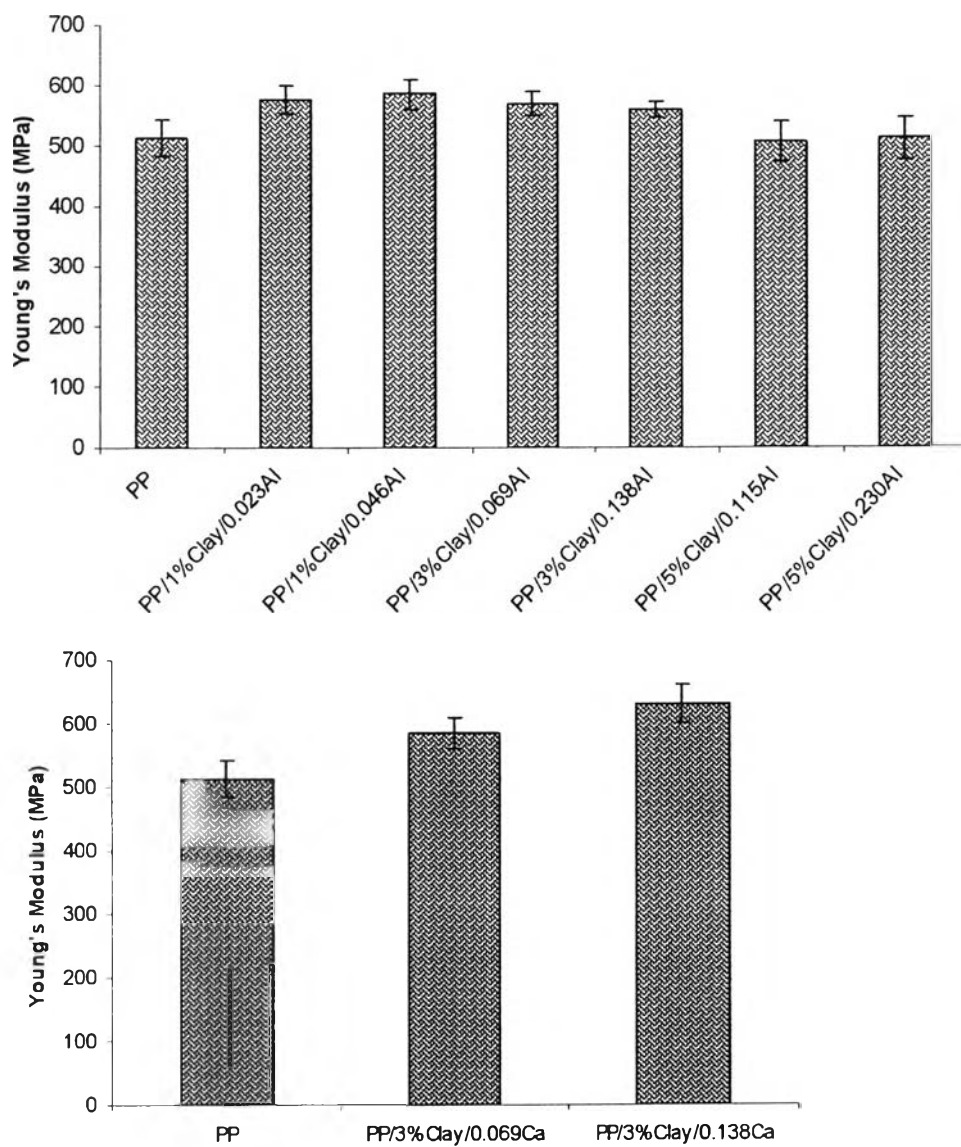


Figure 5.3 Young's modulus of ethylene/carbon dioxide scavenger PP/organo-modified bentonite nanocomposite films

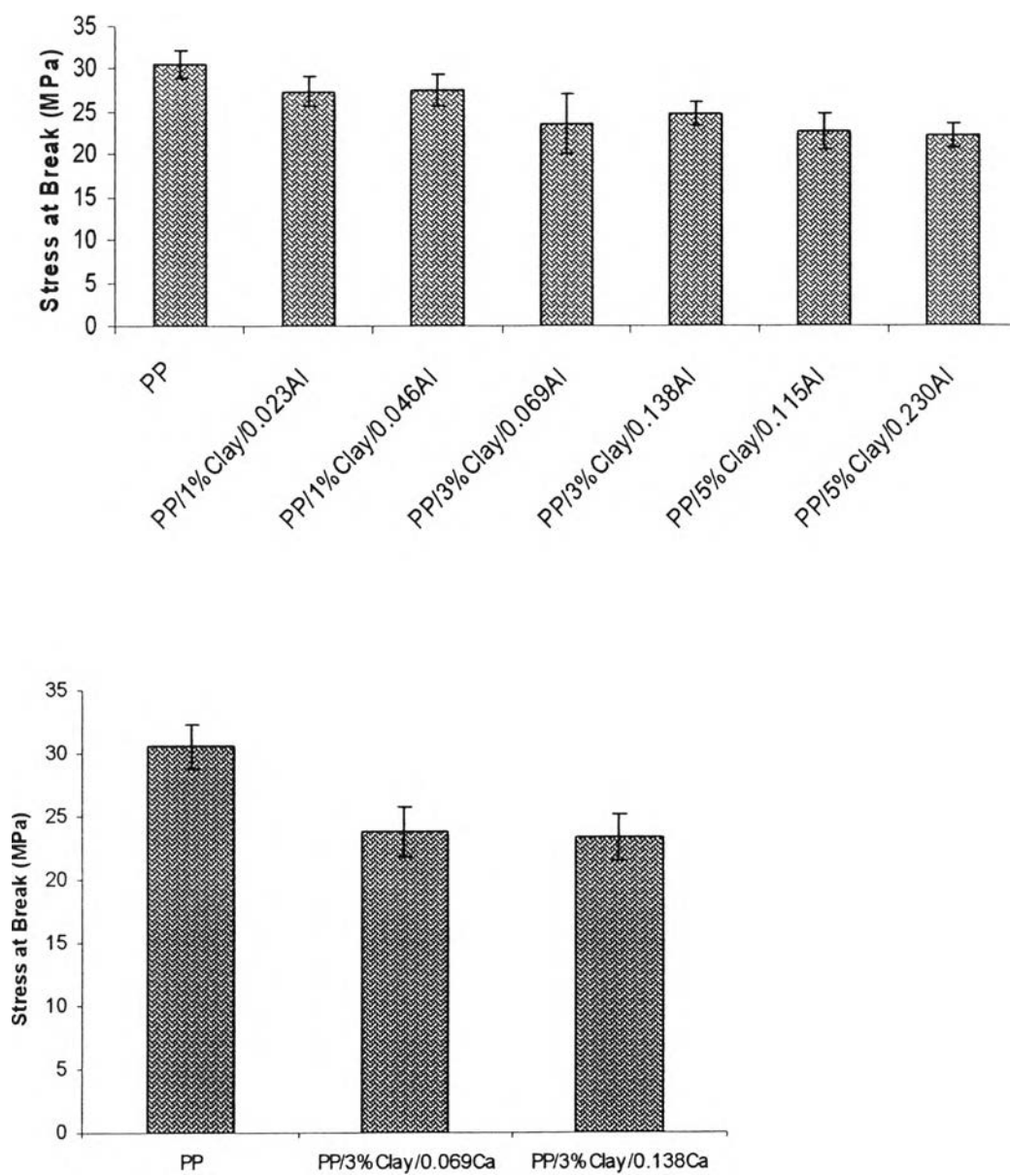


Figure 5.4 Stress at break of ethylene/carbon dioxide scavenger PP/organomodified bentonite nanocomposite films

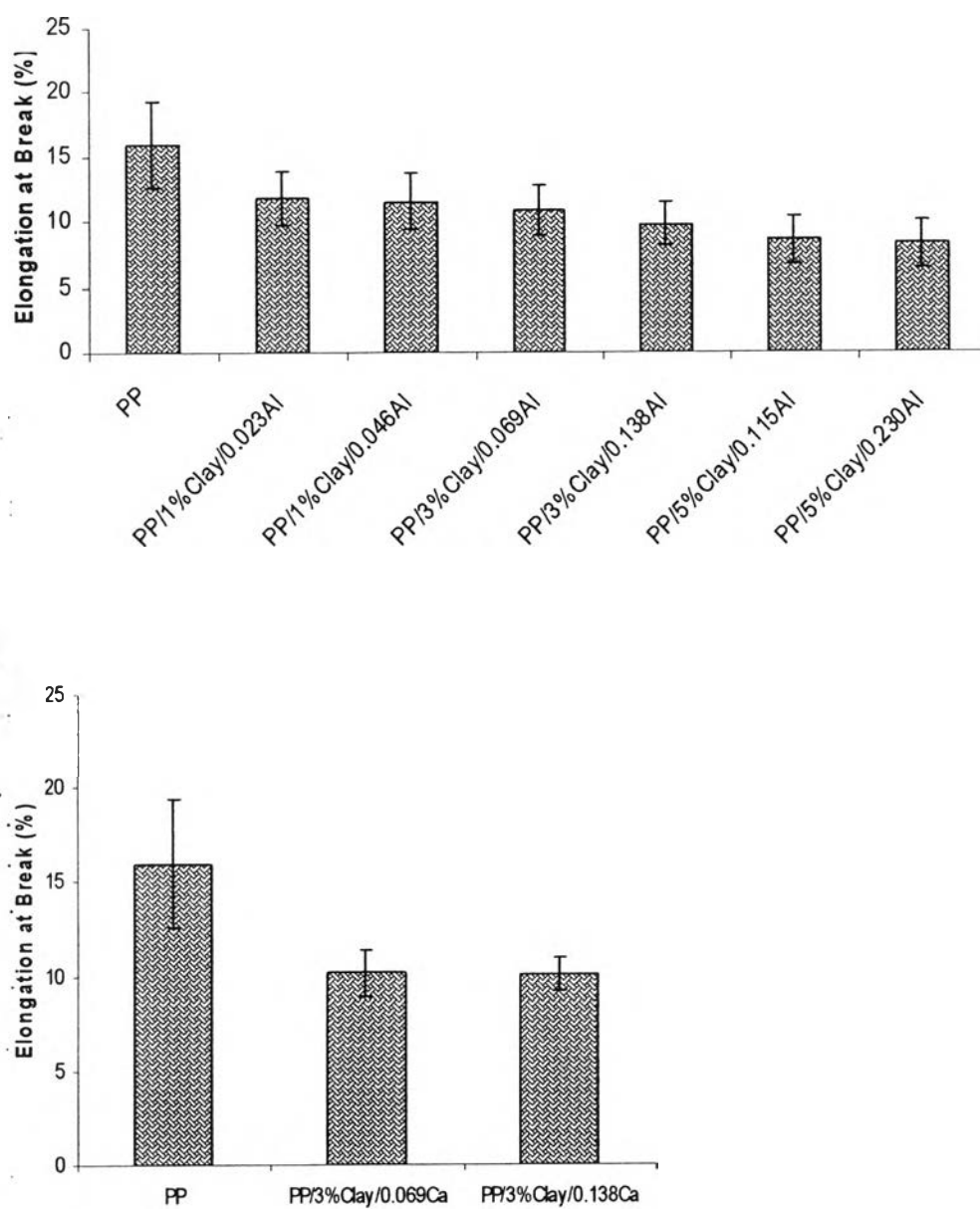
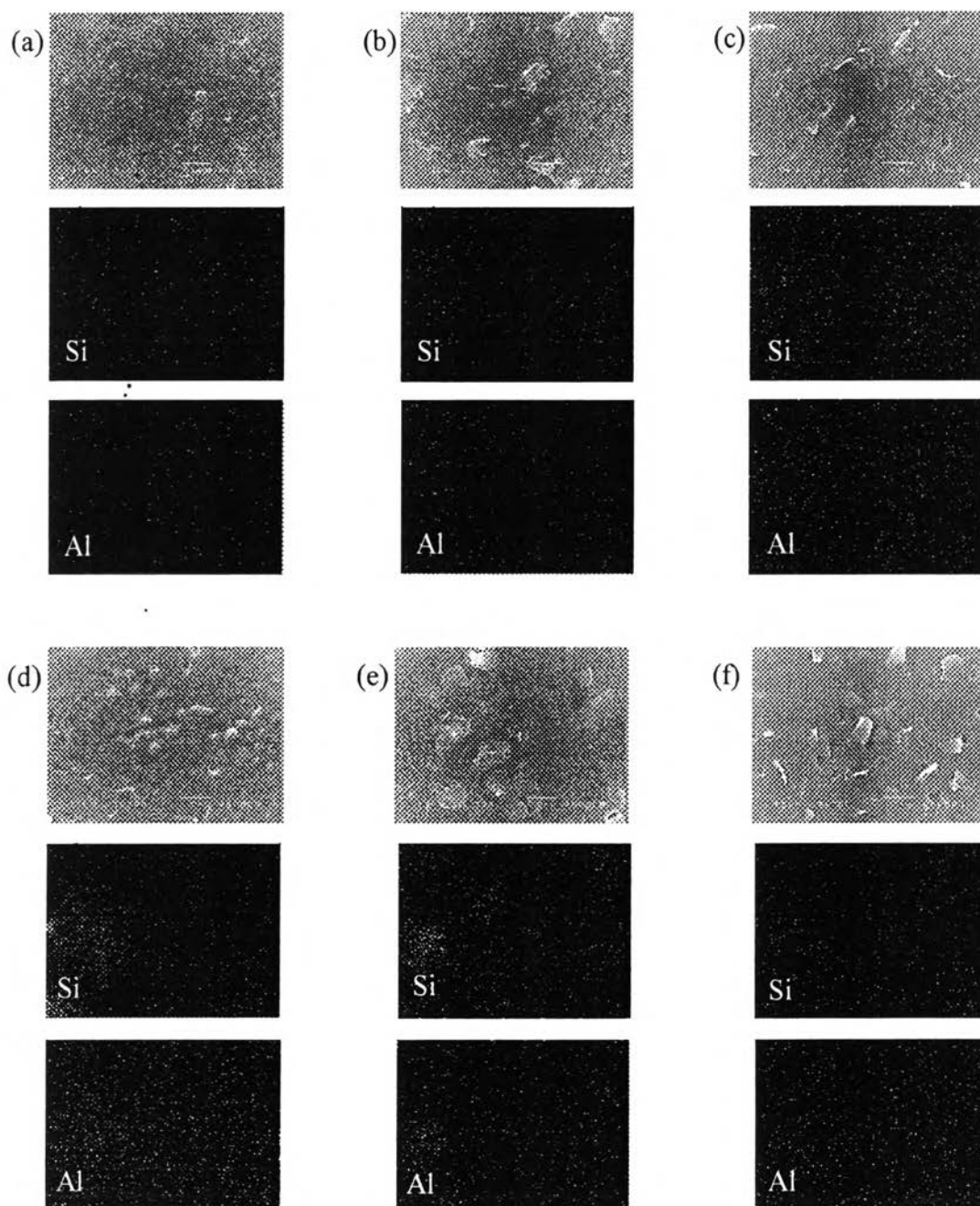


Figure 5.5 Elongation at break of ethylene/carbon dioxide scavenger PP/organo-bentonite nanocomposite films

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

The dispersion of organoclay and aluminum/calcium compound shown in Figure 5.9, aluminium hydroxide system showed better dispersion in PP film. When increasing content of aluminium compounds the agglomeration occurred as the small nodules in the nanocomposite films [10].



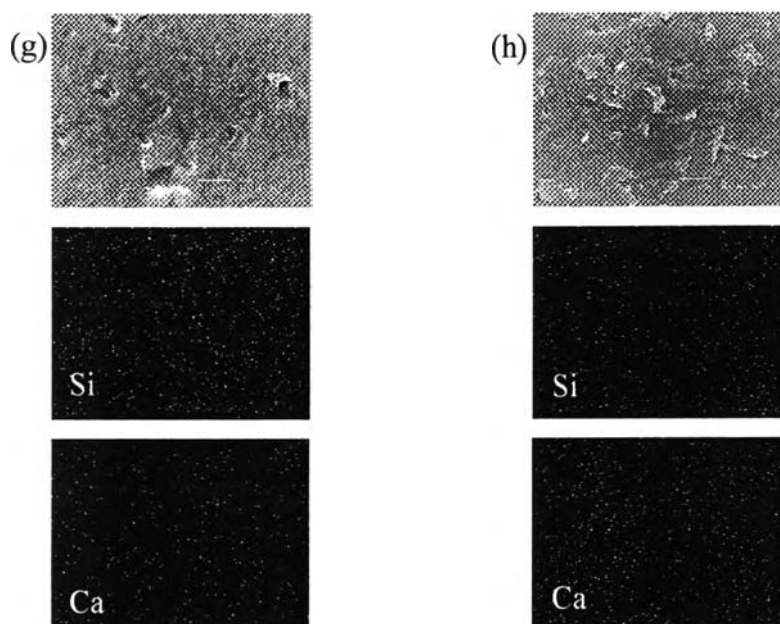


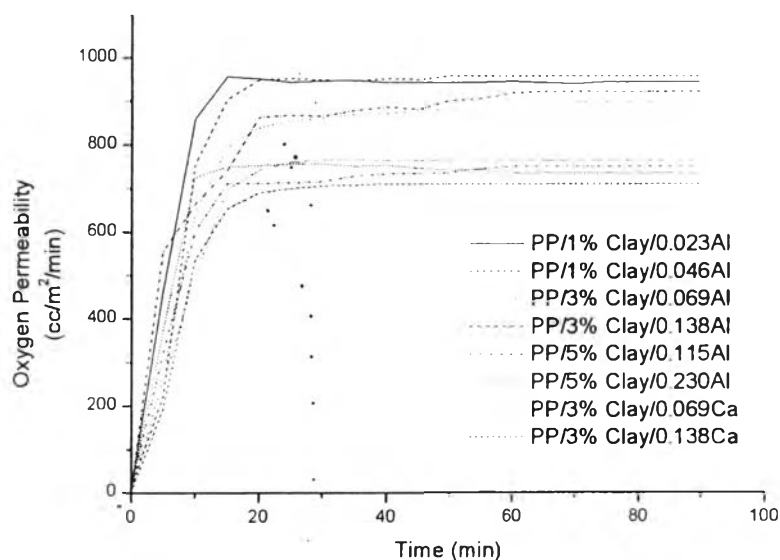
Figure 5.6 SEM images of Si and Al or Ca mapping of ethylene/carbon dioxide scavenger PP/organoclay nanocomposite films (a) PP/1%Clay/0.023Al, (b) PP/1%Clay/0.046Al; (c) PP/3%Clay/0.069Al, (d) PP/3%Clay/0.138Al, (e) PP/5%Clay/0.115Al, (f) PP/5%Clay/0.203Al, (g) PP/3%Clay/0.069Ca, (d) PP/3%Clay/0.138Ca :

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

The oxygen permeability of ethylene and carbon dioxide scavenger PP/organomodified bentonite nanocomposites films shows in Table 5.4 and Figure 5.7. The oxygen permeability of nanocomposites films without scavenger was about 600 cc/m²/day. However, the oxygen permeability of ethylene/carbon dioxide scavenger PP/organomodified-BTN nanocomposites films was higher than that. This reveals that aluminum/calcium compounds may introduce some micro void due to poor compatibility with PP and thus raising higher permeability. Moreover, when increased the content of organoclay and aluminum hydroxide, the oxygen permeability was reduced due to the effect of organomodified-BTN which are believed to increase the barrier properties by creating a maze or tortuous path that retards the progress of the gas molecules through the all of matrix resin [11, 12].

Table 5.4 Oxygen permeability of nanocomposites films

Samples	O ₂ Permeability (cc/m ² /day)
PP	3580
PP/1%Clay/0.023Al	945
PP/1%Clay/0.046Al	958
PP/3%Clay/0.069Al	898
PP/3%Clay/0.138Al	922
PP/5%Clay/0.115Al	751
PP/5%Clay/0.230Al	735
PP/3%Clay/0.069Ca	764
PP/3%Clay/0.138Ca	710

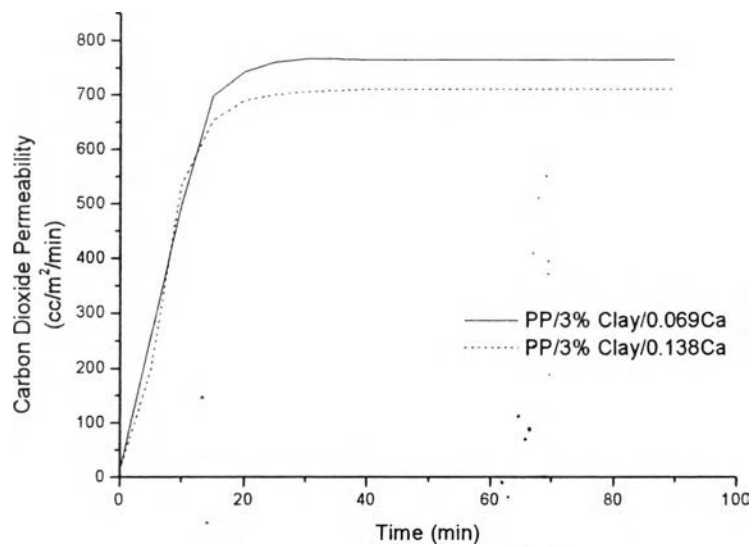
**Figure 5.7** Oxygen permeability of PP/organo-modified bentonite nanocomposites films

F. Carbon Dioxide permeability of carbon dioxide scavenger PP/organo-modified bentonite nanocomposite films

The carbon dioxide permeability of carbon dioxide scavenger PP/organo-modified bentonite nanocomposites films shows in Table 5.5. The incorporation of calcium hydroxide, which is carbon dioxide scavenger, and organo-modified bentonite into PP matrix dramatically reduced amount of carbon dioxide due to the efficiency of clay that enhance gas barrier properties, and gas carbon dioxide were also reduced by carbon dioxide scavenger [13].

Table 5.5 Carbon dioxide permeability of nanocomposites films

Samples	CO ₂ Permeability (cc/m ² /day)
PP	3886
PP/3%Clay/0.069Ca	356
PP/3%Clay/0.138Ca	413

**Figure 5.8** Carbon dioxide permeability of PP/organo-modified bentonite nanocomposites films

G. Ethylene gas reduction of ethylene scavenger PP/organomodified bentonite nanocomposite films

When increased % content of organoclay and aluminum compound into PP films, the concentrations of ethylene were reduced rapidly as the time past by due to aluminum hydroxide acts as ethylene scavenger [14]. It also enhanced the efficiency of organoclay to absorb ethylene.

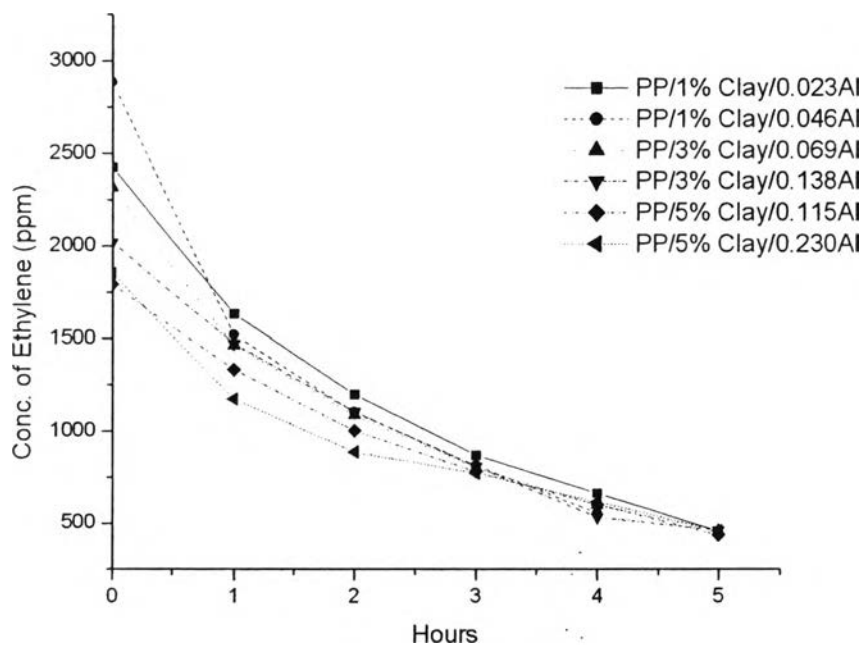


Figure 5.9 Ethylene reduction of ethylene scavenger PP/organomodified-BTN nanocomposites films

5.5 Conclusions

The addition of aluminum or calcium compound into PP slightly increased % crystallinity, melting temperature and crystallization temperature of PP. Young's modulus was improved, but stress at break and elongation at break of the active packaging films were reduced when compare with PP. These due to the agglomeration of organomodified bentonite and aluminum compounds. The oxygen permeability decreases when organoclay and aluminum/calcium compounds were added. Furthermore, carbon dioxide permeability were also reduced due to the efficiency of calcium hydroxide and organomodified-BTN. Moreover, the ethylene reduction was reduced rapidly when increased aluminum compound.

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