



## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Active Packaging

In recent years, new food packaging systems have been developed to remove undesirable substances from the headspace of a package by a physical or chemical absorbent or adsorbent which is incorporated in the packaging material or added into the package as a sachet (Ahvenainen, 2003).

Active packaging is an innovative concept that can be defined as a type of packaging that changes the condition of the packaging to extend shelf-life or improve safety or sensory properties while maintaining the quality of the food (Vermeiren *et al.*, 1999). Examples of active packaging systems are shown in Table 1.

**Table 2.1** Example of some active packaging systems

Type of active packaging system	Substances used and mode of action
Oxygen absorbing	Enzymatic systems (glucose oxidase-glucose, alcohol oxidase-ethanol vapor) Chemical systems (powdered iron oxide, catechol, ferrous carbonate, iron-sulfur, sulfite salt-copper sulfate, photosensitive dye, oxidation, ascorbic acid oxidation, catalytic conversion of oxygen by platinum catalyst)
Carbon dioxide absorbing/emitting	Iron powder-calcium hydroxide, ferrous carbonate-metal halide
Moisture absorbing	Silica gel, propylene glycol, polyvinyl alcohol, diatomaceous earth
Ethylene absorbing	Activated charcoal, silica gel-potassium permanganate, Kieselguhr, bentonite, Fuller's earth, silicon dioxide powder, powdered Oya stone, zeolite, ozone
Antimicrobial releasing	Sorbates, benzoates, propionates, ethanol, ozone, peroxide, sulfur dioxide, antibiotics, silver-zeolite, quaternary ammonium salts

Type of active packaging system	Substances used and mode of action
Antioxidant releasing	BHA, BHT, TBHQ, ascorbic acid, Tocopheryl
Flavor absorbing	Baking soda, active charcoal
Flavor releasing	Many food flavors
Color containing	Various food colors
Anti-fogging and anti-sticking	Biaxially oriented vinylon, compression rolled orientated HDPE
Light absorbing/regulating	UV blocking agents, hydroxybenzophenone
Monitoring	Time-temperature indicators
Temperature controlling	Non-woven microperforated plastic
Gas permeable/breathable	Surface treated, perforated or microporous films
Microwave susceptors	Metallized thermoplastics
Insect repellent	Low toxicity fumigants (pyrethrins, permethrin)

From various types of active packaging system, ethylene and carbon dioxide adsorbing are concerned in this study.

### 2.1.1 Ethylene Scavenging Technology

#### 2.1.1.1 *Effect of Ethylene Gas on Fruits and Vegetables*

Ethylene (C<sub>2</sub>H<sub>4</sub>) acts as plant hormone and plays an important role in the initiation of ripening. The capacity to produce ethylene varies greatly among fruits as shown in Table 2, which those fruits exhibiting moderate to very high production rates and classify as climacteric fruits.

**Table 2.2** Classification of fruits according to their maximum ethylene production rate

Ethylene production rate ( $\mu\text{L kg}^{-1} \text{h}^{-1}$ at 20 °C)	Fruits
Very low: 0.01-0.1	Cherry, citrus, grape, pomegranate, strawberry
Low: 0.1-1.0	Blueberry, kiwifruit, peppers, persimmon, pineapple, raspberry
Moderate: 1.0-10.0	Banana, fig, honeydew melons, mango, tomato
High: 10.0-100.0	Apple, apricot, avocado, plum, cantaloupe, nectarine, papaya, peach, pear
Ethanol emitting	Cherimoya, mamey apple, passion fruit, sapote

The ripening of climacteric fruits is associated with a distinct increase in respiration and ethylene production, the respiration rate will rise up to the climacteric peak and then decline. Such an increase can occur when fruits are attached or separated from the plant. The climacteric fruits, for example, apples, peaches, bananas, mangoes, which changes associated with ripening such as color changes, softening, increase tissue permeability and the development of characteristic aromas. However, in non-climacteric fruits ripening is protracted, and the attainment of the ripe state is not associated with a marked increase in respiration or ethylene production. Typical non-climacteric fruits include citrus, strawberries, and pineapples. Moreover, vegetables do not show a sudden increase in metabolic activity which parallels the onset of the climacteric in fruits, unless sprouting and regrowth is initiated.

Furthermore, when climacteric fruits are exposed to ethylene during their preclimacteric stage, the time to the start of the rising respiration is reduced. The magnitude of the final respiratory rise is controlled by the fruit's endogenous ethylene

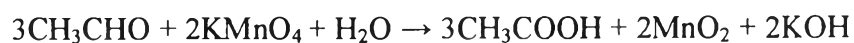
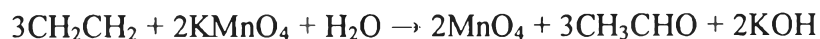
production. A reduction in ethylene production and sensitivity associated with modified atmospheres can delay the onset of the climacteric and prolong the storage life of these fruits. When non-climacteric tissues are exposed to ethylene, the respiration is induced proportional to the ethylene concentration. The respiration rates return to pretreatment level when ethylene is removed. Non-climacteric fruits and vegetables can benefit from reduced ethylene sensitivity and lower respiration rate attributed to modified atmospheres.

The potent effects of ethylene on plant growth, development and senescence mean that this gas can reduce the storage life of fresh fruits and vegetables. Important effects of ethylene include accelerated senescence and loss of green color in some immature fruits and leafy vegetables, accelerated ripening of fruits during handling and storage, russet spotting on lettuce, enhanced the opportunities for pathogenesis, etc.

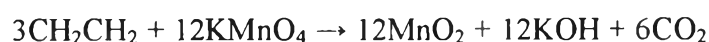
#### *2.1.1.2 Principle of Ethylene Adsorption*

The double bond of ethylene is a very reactive compound that can be altered in many ways. This creates a diversity of opportunities for the removal of ethylene. Ethylene removal media are usually composed of pellet or porous solids such as activated alumina, vermiculite. A number of catalytic oxidizers have been combined with adsorbent to remove the adsorbed ethylene, for example, iodine pentoxide, silver nitrate, potassium dichromate, and potassium permanganate ( $\text{KMnO}_4$ ), each respectively embedded on silica gel. Especially, potassium permanganate, it is a broad-spectrum oxidizing agent that can react with other contaminant gases. To be effective  $\text{KMnO}_4$  must be adsorbed on a suitable carrier with a large surface area such as celite, vermiculite, activated carbon, silica gel, alumina pellets.

The oxidation of ethylene with potassium permanganate can be thought of as a two-step process. Ethylene ( $\text{CH}_2\text{CH}_2$ ) is initially oxidized to acetaldehyde ( $\text{CH}_3\text{CHO}$ ), which in turn is oxidized to acetic acid ( $\text{CH}_3\text{COOH}$ ). Acetic acid can be oxidized to carbon dioxide and water:



Combining all equation, thus:



Potassium permanganate absorber is purple in color but after reacting with ethylene, it turns brown as  $\text{MnO}_4^-$  is reduced to  $\text{MnO}_2$ . Typically, adsorbent materials containing  $\text{KMnO}_4$  cannot be integrated into food-contact packaging but are supplied as blankets, tubes, or sachets because of their toxicity and purple color. Sachets are utilized in individual boxes of fruits or vegetables, whereas blankets and tubes are commonly employed in transport vehicles (Brody, 2001). Different studies have shown that these sachets effectively remove ethylene from packaging, for example, Howard *et al.*, (1994) determined the effect of a gas absorbent on quality of diced onions that were pack in a film package, polyethylene, and stored at 2 °C. The gas absorbent consisted of potassium permanganate and activated alumina formed into small spheres. Adsorbent sphere were enclosed in a spun bonded polyester sachet which prevented bleeding of potassium permanganate in the product. They found that ethylene accumulated to a maximum concentration of 3 ppm (3 day) after processing in samples packed without absorbent, and then declined linearly during the remainder of the experiment. On the other hand, minimal levels of ethylene (<0.1 ppm) were detected in samples packed with absorbent and acceptable quality of diced onions can be retained for 10 days using potassium permanganate gas absorbent.

Another type of ethylene scavenger is based on the adsorption of ethylene on activated carbon and subsequent breakdown by a metal catalyst. In 1992, Abe and Watada studied the effect of charcoal with palladium chloride to remove ethylene gas. It was determined with kiwifruits, bananas, broccoli, and spinach leaves. All samples were chopped into small pieces and placed in a metal tray containing a paper packet of ethylene absorbent and a glass cover. From the results, charcoal with palladium chloride prevented the accumulation of the ethylene and was effective in

reducing the rate of softening in kiwifruits and bananas and of chlorophyll loss in spinach leaves, but not in broccoli. Therefore, removal of ethylene with this absorbent is beneficial for maintain the quality of lightly processed products.

Other ethylene absorbing technologies are based on the inclusion of finely dispersed minerals. Typically, these minerals are local clay or zeolites incorporated into polyethylene (PE) bag which are then used to package fresh product. Although, the finely divided clays may adsorb ethylene, they also create pores within the plastic bag and alter the gas-transmission properties of the bag. Because ethylene diffuses more rapidly through open pore spaces within the plastic than through the plastic itself. Both ethylene and carbon dioxide diffuse out more rapidly and oxygen will enter faster than with a comparable conventional PE film pouch due to the gap in the film. These effects can enhance shelf-life and reduce headspace ethylene concentrations independently of any ethylene absorption. However, even if the minerals do adsorb ethylene, but it is possible that they will lack significant capacity while embedded in plastic films. The ethylene would have to diffuse through the relatively gas impermeable polymeric matrix before contact with the dispersed mineral, thus, greatly slowing any adsorption processes. Once the ethylene has diffused through the plastic film, venting to the outside may be nearly as fast and effective as adsorption by embedded minerals. In addition, commercially available examples of these mineral containing materials are the Orega plastic film (Matsui), Evert-Fresh (Evert-Fresh Co., USA), Peakfresh<sup>TM</sup> (Peakfresh products, Australia), BO film (Odja Shoji Co., Japan), and Profresh<sup>TM</sup> (Europe)

C<sub>2</sub>H<sub>4</sub> scavengers are not yet very successful, probably because of insufficient adsorbing capacity. A large proportion of the fresh fruits and vegetables harvested each year are lost due to fungal contamination and physiological damage (Blidi *et al.*, 1993). The C<sub>2</sub>H<sub>4</sub> adsorbing packaging concepts could possible contributed to an increase in the export of fresh produce.

## 2.1.2 Carbon Dioxide Scavenging Technology

### 2.1.2.1 *Effect of Carbon Dioxide Gas on Fruits and Vegetables*

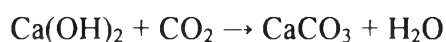
Carbon dioxide (CO<sub>2</sub>) acts both as an inducer and as a suppressor of respiration depending on its concentration in situ, internal oxygen concentration, duration of exposure, the commodity and on temperature, during and subsequent to carbon dioxide exposure (Paris *et al.*, 1994). Therefore, carbon dioxide has been interested or studied to kill, stimulate, inhibit or have no noticeable effect on the growth of microorganisms on flesh foods (e.g. beef, pork, poultry, fish), eggs, fruits and vegetables, depending on the organisms, the concentration of CO<sub>2</sub>, the temperature of incubation, the age of the cell when CO<sub>2</sub> is applied, and the water medium. Generally, most yeasts, molds and bacteria are inhibited by concentrations from 5-50% (v/v gas phase), the inhibition increasing linearly with increasing concentration, however, they are not entirely prevented from growing. Lower concentrations of CO<sub>2</sub> tend to have no effect, or actually stimulate growth, but a high CO<sub>2</sub>-atmosphere can reduce the incidence and severity of certain physiological disorders such as those induced by ethylene (scald of apples and pears) and chilling injury of some commodities (e.g. avocado, citrus fruits, chili pepper). On the other hand, CO<sub>2</sub> levels beyond those tolerated by the commodity can induce physiological disorders, such as brown stain on the lettuce, internal browning and surface pitting of some fruits, and blackheart of potato. In addition, elevated CO<sub>2</sub> levels can inhibit, promote or have no effect on C<sub>2</sub>H<sub>4</sub> production of fruits. However, CO<sub>2</sub> have been shown to be a competitive inhibitor of C<sub>2</sub>H<sub>4</sub> action, delaying fruit ripening by displacing C<sub>2</sub>H<sub>4</sub> from its receptor site. The respiration rate of most root and bulb type vegetables when stored under elevated CO<sub>2</sub> level is stimulated, probably as an injury response that leads to further disorder and shortened life (Robertson, 1993).

Carbon dioxide (CO<sub>2</sub>) is also formed in some food due to deterioration and respiration reactions. Therefore, produced CO<sub>2</sub> has to be removed from the package to avoid food deterioration and/or package destruction due to the accumulation of CO<sub>2</sub> in the packages causes ballooning or even bursting. The CO<sub>2</sub> absorber might be useful and it is mentioned in next topic.

### 2.1.2.2 Principle of Carbon Dioxide Adsorption

Carbon dioxide absorbents usually play a beneficial role in food packaging. For example, fresh roasted coffee can release considerable amounts of CO<sub>2</sub> due to the Strecker degradation reaction between sugars and amines (Labuza *et al.*, 1988). Unless removed, the generated CO<sub>2</sub> can cause the packaging to burst due to the increasing internal pressure. Another CO<sub>2</sub>-producing food product is kimchi, a general term for fermented vegetables such as oriental cabbage, radish, green onion, and leaf mustard mixed with salt and spices. Because kimchi cannot be pasteurised for its sensory quality, the fermentation process still continues with the concomitant production of CO<sub>2</sub>. Therefore, Lee *et al.*, (2001) examined some physical absorbents of carbon dioxide and tried to find an appropriate condition of these absorbents which was incorporated into kimchi packaging.

The reactant commonly used to scavenge CO<sub>2</sub> is calcium hydroxide, which, at a high enough water activity, reacts with CO<sub>2</sub> to form calcium carbonate:



A disadvantage of this CO<sub>2</sub> scavenging substance is that it scavenges carbon dioxide from the package headspace irreversibly and results in depletion of CO<sub>2</sub>, which is not always desired. In the case of packaged kimchi, decreasing of CO<sub>2</sub> in kimchi juices causes loss of the product's characteristic fresh carbonic taste. Therefore, reversible absorption or adsorption by physical sorbents such as zeolites and active carbon may be an alternative.

Carbon dioxide scavengers are often commercialized as a sachet with a dual function, both O<sub>2</sub> and CO<sub>2</sub> scavenging. For example, FreshLock<sup>®</sup> or Ageless<sup>®</sup>E (Mitsubishi Gas Chemical Company, Japan), containing Ca(OH)<sub>2</sub> is used for storing coffee. Multiform Desiccants Incorporated has developed a CO<sub>2</sub> absorbing sachet that is composed of a porous envelope containing CaO and a hydrating agent such as silica gel on which water is adsorbed. The water given off by the supersaturated silica gel reacts with calcium oxide and produces calcium



hydroxide, which then reacts with CO<sub>2</sub> to form calcium carbonate (Ozdemir *et al.*, 2004).

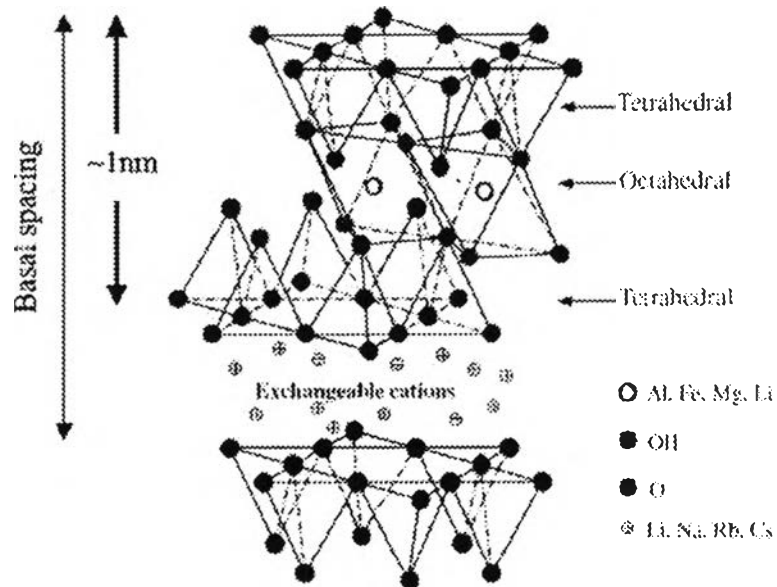
In 2006, Charles *et al.* studied the absorption kinetics of commercial carbon dioxide scavenger sachet which is calcium hydroxide, ATCO<sup>®</sup> CO-450. The scavenger sachets were placed in polyvinylidene chloride film (PVDC) pouches and store at 20 °C with CO<sub>2</sub> initial levels of 50 kPa. At 0% relative humidity (RH), no significant gas adsorption occurred indicating that ATCO<sup>®</sup> CO-450 was not self-activating and needed moisture to be efficient. Thus, the experiments were conducted at 100%. In this condition, CO<sub>2</sub> residual changed with time. The amount of CO<sub>2</sub> absorbed by the scavenger was 8 and 70ml after 1 and 10 hours, respectively. The saturation was reached after approximately 150 hours with the capacity of 434 ± 30ml. In ATCO<sup>®</sup> CO-450, the CO<sub>2</sub> absorption proceeded due to carbonation, and so in FreshLock<sup>®</sup> or Ageless<sup>®</sup>E sachets which were both composed of calcium hydroxide.

As mentioned before, dispersed clay mineral takes many beneficial roles in the term of scavenging system. Therefore, it will be concerned and studied in this present work by embedding ethylene and carbon dioxide scavenging modified nanoclay into polypropylene to fabricate the nanocomposite films. The clay mineral using in this research is bentonite which was discussed in the following topic.

## **2.2 Organobentonite for Polymer Nanocomposites**

Clay minerals, or phyllosilicate, have been use as inorganic fillers for the polymer composites to reduce the cost or to provide them special properties such as modulus, hardness, thermal stability, thickening, etc. Many kinds of clays such as bentonite, kaoline, talc, mica. However, bentonite is interested in this study.

Bentonite is a clay mainly composed of montmorillonite which is a 2:1 type aluminosilicate. Its crystalline structure presents an alumina octahedral layer between two tetrahedral of silica. The isomorphous substitutions require cations, denominated exchange cations, to compensate the negative charges in their laminar edges (Rodriguez-Sarmiento *et al.*, 2001).



**Figure 2.1** Structure of 2:1 phyllosilicates (Sorrentino *et al.*, 2007).

Polymer nanocomposites, especially polymer-layered silicate nanocomposites, represent the alternative filler for polymers due to they exhibit markedly improved properties when compared with the pure polymer or conventional composites. However, the differences of the surface energy and the elasticity between the dissimilar materials induce the decrement of some properties such as toughness, stiffness, strength, etc. Therefore, to reduce the difference of surface energy, clay mineral are usually treated with coupling agents and to reduce the internal stress on the interface, they should be prepared to as smaller size as possible (Lee *et al.*, 2004). In order to prepare nanocomposites, several approaches are used: (i) solution and drying method, (ii) monomer intercalation and polymerization method, (iii) polymer intercalation and compounding method.

### 2.2.1 Solution and Drying Method

Organoclay is swelled in the solution and the nano-sized clay mineral is dispersed in the polymer matrix during the drying process. In 2001, Y.I. Tien and K.H. Wei choose 3-amino-1-propanol, 3-amino-propandiol, tris(hydroxymethyl) aminomethane, and dodecylamine, which were treated with hydrochloric acid and

contained one to three hydroxyl groups and one amine group for modifying montmorillonite and react with polyurethane prepolymer. These compounds are noted as reactive swelling agent. They have dual functions, which amine group converted into onium form to replace the metal ions in the gallery of silicate for intercalation, and the hydroxyl functional groups react with the isocyanate groups of the polyurethane prepolymer. Therefore, result in an ultrahigh efficiency in enhancing the mechanical properties of polyurethane.

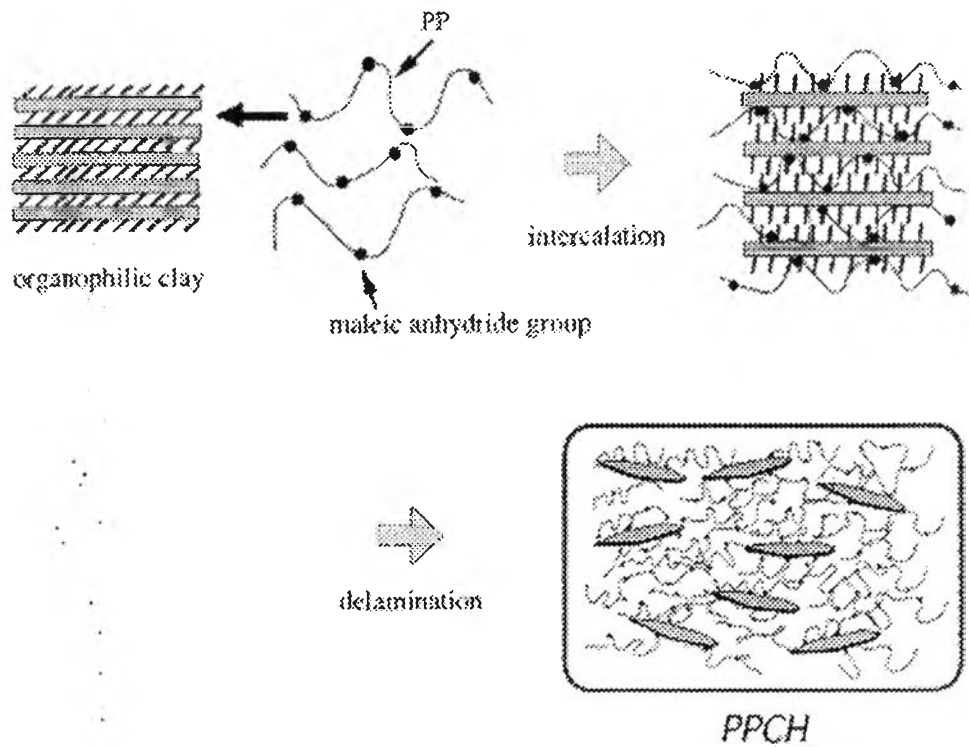
### 2.2.2 Monomer Intercalation and Polymerization Method

Organoclay is swollen with in the liquid monomer so as the polymer formation can occur between the intercalated sheets. Polymerization can be initiated by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step of the monomer (Sinha *et al.*, 2003). In 2004, Suh *et al.* studied the properties and formation mechanism of nanocomposites by using unsaturated polyester (UP), the styrene monomer, unsaturated polyester linear chain and organophilic-treated montmorillonite (MMT) exist together in the system. In other word, the mixture of UP and organophilic-treated MMT were prepare in the first step, then, the styrene monomer was added to these pre-intercalates of UP/MMT. Finally, all mixture were cured and preformed for many hours. In addition, they also found that the styrene monomer moves more easily than uncured UP linear chains, and it diffuses to the gallery of the MMT intercalated with UP to an extent or well-dispersed portion which increases with the mixing time.

### 2.2.3 Polymer Intercalation and Compounding Method

The delamination of the organoclay is performed through polymer melt penetration into the gallery during mechanical mixing. In the case of dissimilar materials, polymer and organoclay, compatibilizer is commonly used and plays an important role in this method. In 1998 and 2000, Hasegawa *et al.* prepared a PP-clay hybrid (PPCH) by using a functional oligomer as a compatibilizer, in which the silicate layers of the clay were dispersed uniformly to the nanometer level. In this case the PPCHs consisted of PP, the functional oligomer, and organophilic clay. In addition, they also found that PP with functional groups was intercalated into the

interlayers of the organophilic clay, as well as the functional oligomer. The PPCHs was prepared in twin-screw extruder by maleic anhydride modified PP (PP-MA), and montmorillonite which intercalated with octadecylammonium. The results showed that modulus and strength of the PPCHs increased as the clay content increased.



**Figure 2.2** The schematic figure of the clay dispersing process.

In addition, the polymer-clay nanocomposites synthesized by the above methods are classified into intercalated and exfoliated (delaminated) according to the state of the multilayer of clay. The term intercalation describes the case where a small amount of polymer chain is inserted into the gallery of the clay minerals, but it preserves the well-ordered multilayer structure of silicate or the separation between clay platelets is less than 20-30 Å. On the other hand, exfoliation or delamination occurs when polymer further separates the clay platelets, e.g. by 80-100 Å or more, where the interaction between the silicate monolayers no longer exists. A well-delaminated and dispersed nanocomposite consists of delaminated platelets distributed homogeneously in the polymer.

Incidentally, Varothai Y. (2006) studied the polypropylene/organo-modified clay nanocomposites, which were prepared for active packaging films. Ethylene scavenger which is aluminum hydroxide was also incorporated in these films as an ethylene scavenger active packaging to extend the shelf-life of fresh fruits and vegetables. Na-bentonite was treated with surfactant (DOEM) in order to prepare organomodified bentonite, and then, it was compounded with polypropylene by compatibilizer (Surlyn® ionomer). Aluminum hydroxide and aluminum acetate were added to the composites to enhance the ethylene removal capacity. The result shows that gas permeability reduced when only small amount of organomodified bentonite content were added and it is more suitable to extend the self life of fresh fruits and vegetables than the films which were incorporated by both organomodified clay and aluminum hydroxide. Therefore, this is an important point for further study. In this present work, 3-aminopropyl-trimethoxysilane was added in the experiment. This silane acts as surface treatment to stabilize the exfoliated state in the nanocomposites (Wang *et al.*, 2006). The organobentonite was treated with both 3-aminopropyl-trimethoxysilane and aluminum hydroxide, due to the aim which try to attach this ethylene scavenger to nanoclay before compound with polypropylene to be nanocomposites pellets. Moreover, calcium hydroxide as a carbon dioxide scavenger was incorporated into nanoclay which was coalesced with organomodified bentonite and polypropylene to investigate and improve the behavior as the scavenging system of the nanocomposites active packaging film.