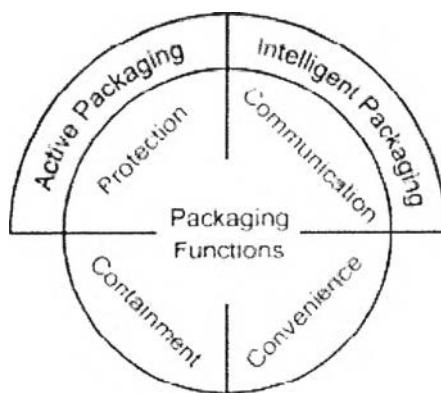


**CHAPTER II**  
**THEORETICAL BACKGROUND AND LITERATURE REVIEW**  
**REFERENCES**

**2.1 Smart Packaging**

According to its definition on Britannica Online Encyclopedia ([www.britannica.com](http://www.britannica.com)), smart packaging is a packaging of food, which offers several properties that satisfy the special needs of some foods. Its model (Figure 2.1) is an association with an active and an intelligent function. For example, certain packages made with oxygen-absorbing material can prevent the oxidation of oxygen-sensitive products because the materials are capable of removing oxygen inside of them. Moreover, a temperature-sensitive film shows an abrupt change in gas permeability when it is subjected to a temperature above or below a set constant.

Since such a smart packaging can help controlling the atmosphere of a food product, it is very useful in creating conditions which are able to extend a food storage life. The packaging material generally used for foods may be categorized as flexible (papers, thin laminates, and plastic films), semi-rigid (aluminum foil, laminates, paperboard, and thermoformed plastics), and rigid (metals, glasses, and thick plastics). Plastics are extensively used in food packaging because of being relatively cheap, lightweight, and easy to be formed into desired shapes.



**Figure 2.1** Model of packaging function.

There are tremendous kinds of active and intelligent packaging as below (Table 2.1):

**Table 2.1** Examples of active and intelligent packaging

<b>Active Packaging</b>	<b>Intelligent Packaging</b>
Anti-microbial	Time-temperature indicators
Ethylene scavenging	Microbial spoilage sensors/indicators
Heating/cooling	Physical shock indicators
Moisture absorbing	Leakage sensors
Odor and flavor absorbing/releasing	Allergen sensors
Oxygen scavenging	Microbial growth sensors
Spoilage retarder	Pathogens and contaminants sensors

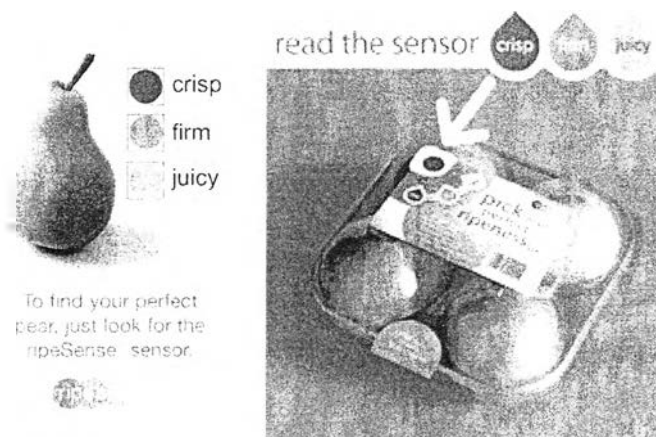
As Murphy *et al.* (2003) mentioned while maintaining the quality of the packaged products, an active packaging was actively changed the condition of the packaged food to either extend shelf-life of products or to improve safety and sensory properties. Conversely, an intelligent packaging was employed to monitor the condition of packaged foods to give some information in terms of quality of the packaged food during storage and transportation.

For example, regarding an active film, a modified atmosphere packaging (MAP) was capable of prolonging the shelf-life of product and it was the fastest emerging technology for food packaging. Statistically, the numerous amounts of packed products in Europe using MAP technology were likely to exceed 20 billion a year. The MAP uptake was currently rapid in markets i.e. fish, fruits and vegetables as well as fresh meat. In addition, some people strongly held that the active packaging product would be achieved from combination with MAP, so the MAP needed the use of barrier materials for packaging including transparent flexible films by reason of providing benefits from combination with the active packaging (Murphy *et al.*, 2003). Apart from the MAP, a recent report also demonstrated that there were several tremendously available active packaging segment dominated by oxygen

scavengers, moisture absorbers and barrier packaging product, accounting for 80% of the market (Robinson and Morrison, 2010).

With regard to an intelligent packaging, there were various kinds of them, such as TTIs (Time Temperature Indicators) and TTBs (Time Temperature Biosensors). Aside from the temperature sensors, there were other types of sensors such as spoilage indicators, which were still on the early stages of development. However, pathogen indicators, which had particular detection of a specific sort of pathogen were still on the onset stages of development as well. (Murphy *et al.*, 2003)

According to TIME magazine (2004), it reported a new sensor for fruit ripeness named “*ripeSense*<sup>®</sup>” (Figure 2.2). The sensor was capable of indicating the ripeness of fruit by changing its color in response to deterioration of fruits. The performance of this sensor helped enabling consumers to easily make a decision to purchase products at their preferred degree of ripeness. Therefore, this sensor was able to be used as a smart choice for the monitor of agricultural products by the naked eyes.

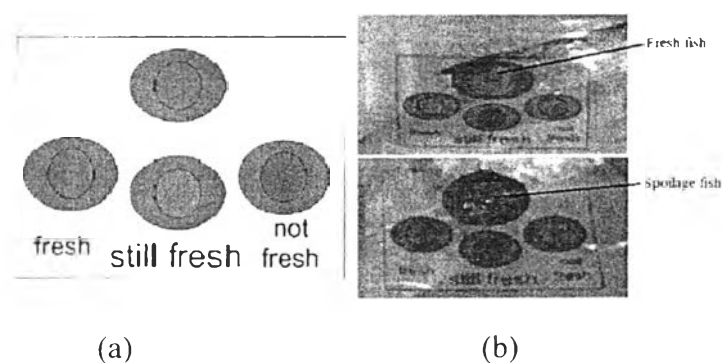


**Figure 2.2** Ripeness sensor from RIPSENSE<sup>®</sup>. (<http://www.ripesense.com>)

## 2.2 Intelligent Film for Fish Freshness Indicator

An intelligent or sensor film is useful for facilitating decision making to consumers because it provides a great deal of essential information on quality and safety, and particular warning possible problems to consumers (Rukchon *et al.*, 2011). In the case of fish products, both volatile and non-volatile amines are formed during the breakdown of their freshness. Total volatile basic nitrogen (TVBN) plays a significant role in being a marker indicating fish freshness it is, therefore, a reliable method for assessing the quality of fish during storage.

Kuswandi *et al.* (2012) showed a new colorimetric label for fish spoilage based on polyaniline (PANI) film. Its usefulness was a chemical sensor, of which the function was pH-sensitive film, for a real-time monitor on the breakdown products in the headspace area of packaged fish. The visible color (Figure 2.3) of PANI film changed from green (freshness indicator) to blue (spoilage indicator) in response to total volatile basic nitrogen (TVBN) or amine released during the spoilage of fish. The outset stage of color change was approximately after 8 hr at room temperature. The color change of PANI film toward spoiling fish originated from the occurrence of the protonation-deprotonation process in PANI film. From the mechanism, it was concluded that there was the presence of an effective proton migration, which enabled protons from the green emeraldine (proton donor) to change into blue emeraldine base (proton acceptor).



**Figure 2.3** (a) Sensor design and (b) its application as a smart packaging for milkfish.

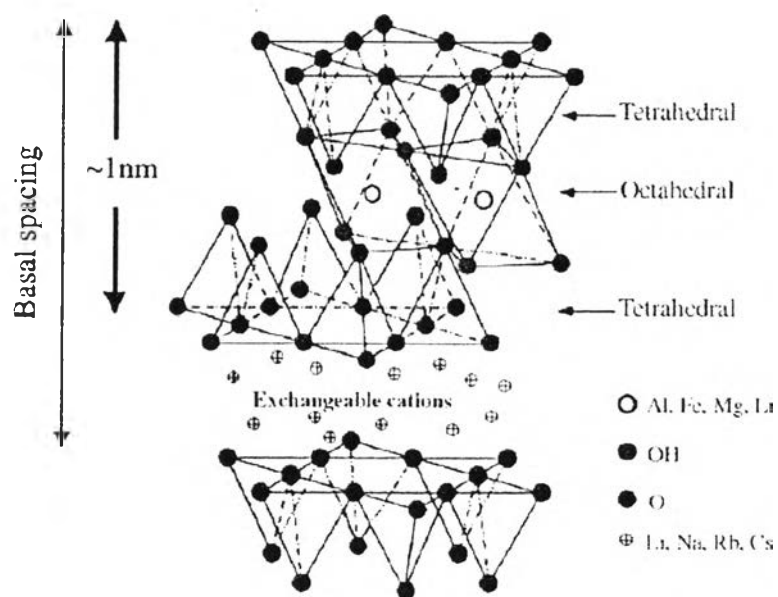
## 2.3 Overview of Polymer-Clay Nanocomposites

According to [www.nanocompositech.com](http://www.nanocompositech.com), polymer nanocomposites are advanced materials divided into three new classes namely polymer/clay nanocomposites, polymer/metal nanocomposites, and polymer/carbon-nanotube nanocomposites. Polymer/clay nanocomposites are strongly highlighted on the thesis.

Among materials, polymer/clay nanocomposites have recently drawn the attention from researchers due to their remarkable improvements on properties of materials compared to conventional micro- or macro-composites as well as pure polymers. The resulting improvements are high moduli, increased strength and heat resistance, decreased gas permeability and flammability, including increased biodegradability of biodegradable polymers.

### 2.3.1 Clay Chemistry

Clay minerals are also considered as layer silicates molecules, which belong to same common family of 2:1 layered or phyllosilicates, because their crystal structure consists of layers. The layers are built up of two tetrahedrally-coordinated silicon atoms connected to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide (Figure 2.4). The layer thickness is about 1 nm, whilst the lateral dimensions of these layers depending upon the particular-layered silicate which may vary from 30 nm to many microns or larger. Moreover, stacking of the layers causes a rectangular van der Waals discrepancy between the layers so-called *gallery* or *interlayer*. Certain isomeric replacements within the layers, such as  $\text{Al}^{3+}$  substituted by  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$ , generate negative charges counterbalanced by alkali and alkaline earth cations located inside the galleries (Table 2.2). The cation exchange capacity (CEC, meq/100 g) used to characterize a type of layered silicate and considered as an average value over the whole crystal is not locally constant, yet varies from layer to layer. (Ray and Okamoto, 2003)



**Figure 2.4** The Structure of 2:1 phyllosilicates. (Ray and Okamoto, 2003)

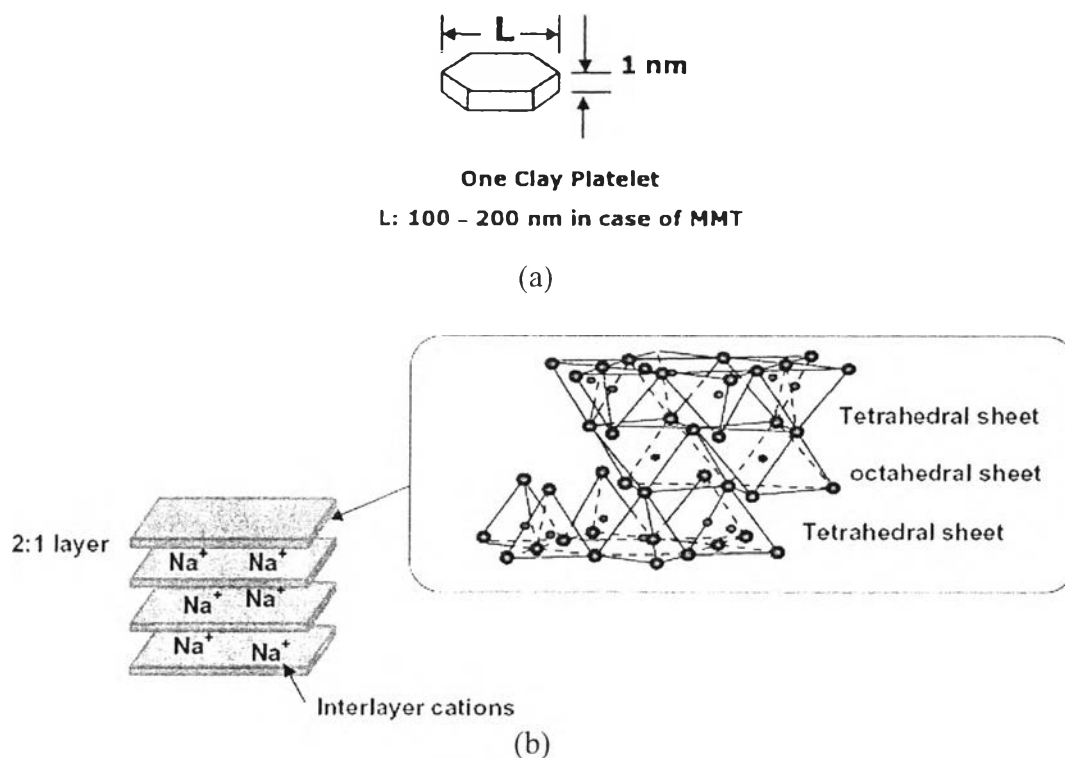
**Table 2.2** Ions found in phyllosilicate minerals (University of New Hampshire, 1998)

Ions found in Phyllosilicate Minerals								
Common constituents			Occasional constituents			Cations found in interlayer spaces		
ion	radius	$r_c/r_o$	ion	radius	$r_c/r_o$	ion	radius	$r_c/r_o$
$O^{2-}$	0.135	-	$Ni^{2+}$	0.074	0.55	$Na^+$	0.101	0.75
$Si^{4+}$	0.040	0.30	$Ti^{4+}$	0.060	0.44	$K^+$	0.134	1.00
$Al^{3+}$	0.055	0.41	$Zn^{2+}$	0.057	0.42	$Cs^+$	0.163	1.24
$Fe^{2+}$	0.080	0.59	$Mn^{2+}$	0.083	0.61	$Ca^{2+}$	0.105	0.78
$Fe^{3+}$	0.067	0.54	$Mn^{3+}$	0.072	0.53	$Ba^{2+}$	0.140	1.03
$Mg^{2+}$	0.078	0.58	$Mn^{4+}$	0.052	0.39	$Sr^{2+}$	0.118	0.87
			$Li^+$	0.076	0.56	$H_2O$	0.145	
			$Cr^{3+}$	0.065	0.48	$NH_4^+$	0.143	
			$Cu^+$	0.095	0.70			

, where  $r_c$  is hydrated radius of the exchange cation;  $r_o$ , ionic radius of the oxygen atom.

### 2.3.2 Sodium Bentonite

The bentonite clay, widely known as sodium bentonite, is rich in montmorillonite. The bentonite is nano-structured and nano-porous mineral of smectite group (Hayati-Ashtiani, 2011). Seeing that montmorillonite, the most-used clay in wide range of applications (Jaber and Miché-Brendlé, 2008), is the major composition of bentonite and has an effect on the whole properties and applications of bentonite, montmorillonite and bentonite sometimes interchange names. (<http://www.aboutclay.com>)



**Figure 2.5** Schematic representation (a) and framework (b) of sodium bentonite. (Ray and Okamoto, 2003; Jaber and Miché-Brendlé, 2008)

**Table 2.3** The percent composition of bentonite (<http://www.bentoniteclay9.com>)

Compositions	Percent
SiO <sub>2</sub>	74.25
Al <sub>2</sub> O <sub>3</sub>	13.56
Fe <sub>2</sub> O <sub>3</sub>	3.90
TiO <sub>2</sub>	0.87
H <sub>2</sub> O	0.67
K <sub>2</sub> O	0.53
CaO	0.38
MgO	0.33
P <sub>2</sub> O <sub>5</sub>	0.02
MnO	0.01
Cr	42 ppm
Zn	23 ppm
Ge	4.5 µg/g

### 2.3.3 Structure and Properties of Clay

Clays, which are the most generally used-layered silicates, have two genres of structure: tetrahedral- and octahedral-substituted. The negative charge is located on the surface of silicate layers in case of tetrahedrally-substituted layered silicates; thereby, the polymer matrices are able to readily react with these rather than with octahedral-substituted materials.

It depends on the structure and chemistry for these layered silicates in Figure 2.4 and 2.5 as well as Table 2.3 and Table 2.4, respectively. There are two remarkable characteristics of layered silicates, which are commonly determined. Both are the ability of the silicate particles to disperse into individual layers and the ability of them to adjust surface chemistry via ion-exchanged reactions with organic and inorganic cations. The characteristics are actually intercalated resulting from the dependence of interlayer cations on the degree of dispersion of layered silicates in a polymer matrix.



**Table 2.4** Chemical formula and characteristic parameter of commonly used 2:1 phyllosilicates (Ray and Okamoto, 2003)

2:1 phyllosilicates	Chemical formula	CEC (meq/100 g)	Particle length (nm)
Monmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110	100 -150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200-300
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	86.6	50-60

, where M, monovalent cation;

$x$ , degree of isomorphous substitution (between 0.5 and 1.3).

### 2.3.4 Types of Polymer/Clay Nanocomposites

#### *2.3.4.1 Types of Polymers used for nanocomposites preparation with clay*

Various polymers feasibly used for preparation of nanocomposites are conventionally divided as following:

(a) Vinyl polymers including the vinyl addition polymers derived common monomers like methyl methacrylate as well as the selective polymers like poly(vinyl alcohol)

(b) Condensation (step) polymers: several technologically-crucial polycondensates have been employed in preparation of nanocomposites i.e. polyamides, polycarbonate, epoxy polymer resins (EPR), etc.

(c) Polyolefins such as polyethylene, polypropylene, polybutadiene, etc.

(d) Specialty polymers including the N-heterocyclic polymers like polypyrrole (PPY) and polyaromatics such as polyaniline (PAN)

(e) Biodegradable polymers such as polylactide, aliphatic and unsaturated polyester, as well as polyhydroxy butyrate, etc.

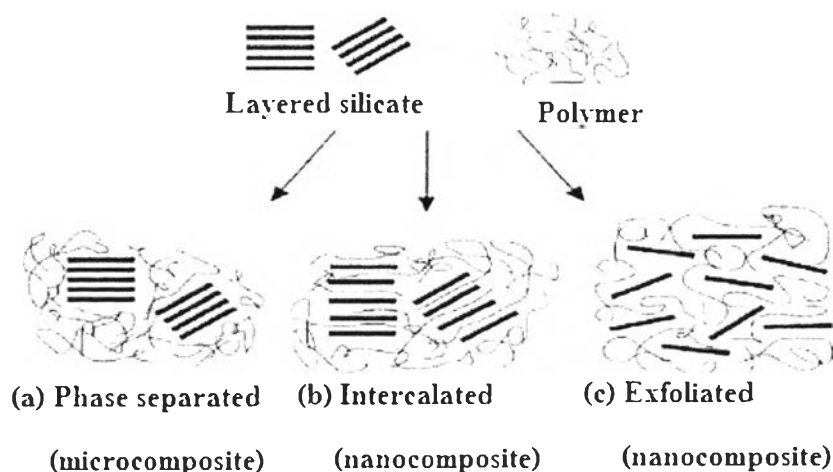
#### *2.3.4.2 Types of Polymer/Clay Nanocomposites*

Generally, there are three main types of polymer/clay nanocomposites, which are thermodynamically accomplishable. Their types depend on the strength of interfacial between the layered silicates (modified or not) and the polymer matrix (Ray and Okamoto, 2003) on the grounds of the nature of the composition used (clay, organic cation, and polymer matrix), and the preparation approach (Alexandre and Dubois, 2000)

(a) Phase-separated nanocomposites: a phase-separated composite (Figure 2.6 (a)) is obtained when the polymer cannot intercalate between the silicate sheets. Its properties are on the same range as conventional micro-composites. (Alexandre and Dubois, 2000)

(b) Intercalated nanocomposites: the insertion of a polymer matrix into the layered silicate structure (Figure 2.6 (b)) takes place in a crystallographically regular function, regardless of the clay to polymer ratio. Commonly, intercalated nanocomposites are interlayer by a few molecular layers of polymer. Properties of composites generally resemble those of ceramic materials. Conceptually, the intercalated and the flocculated nanocomposites are the same but silicate layers are occasionally flocculated as a result of an edge-edge interaction of hydroxylated of the silicate layers. (Ray and Okamoto, 2003)

(c) Exfoliated nanocomposites: an average distance (Figure 2.6 (c)) between the individual clay layers separated in a continuous polymer matrix depends on the clay loading. The content of clays added into nanocomposites is usually much lower than that of an intercalated nanocomposites (Ray and Okamoto, 2003).



**Figure 2.6** Scheme of various types of composites derived from interaction between clay and polymer:

- (a) phase-separated microcomposite; (b) intercalated nanocomposite;
- (c) exfoliated nanocomposite. (Alexandre and Dubois, 2000; Henriette, 2009)

### 2.3.5 Preparative Approaches of Polymer/Clay Nanocomposites

The approaches are divided into three main ways depending on the the starting materials and processing techniques as below: (Ray and Okamoto, 2003)

#### 2.3.5.1 Pre-polymer from solution or intercalation of polymer

This way is based on a system of solvent where the pre-polymer or the polymer is soluble and the silicate layers are swellable. First of all, the layers is swollen in a solvent (water, toluene, or chloroform) and then mixed with the polymer. Consequently, the solvent within the interlayer is replaced and intercalated by the polymer chains. Indeed, the polymer/clay nanocomposites remaining the intercalated structure also rely on the removal of solvent.

#### 2.3.5.2 In situ intercalative polymerization method

The layered silicates are swollen within the liquid monomer. Thereby, the formation of polymer is able to happen between the intercalated galleries. Either heat or radiation, the diffusion of a suitable initiator, or an organic

initiator or catalyst fixed via cation-exchange inside the interlayer before the swelling step can initiate the polymerization.

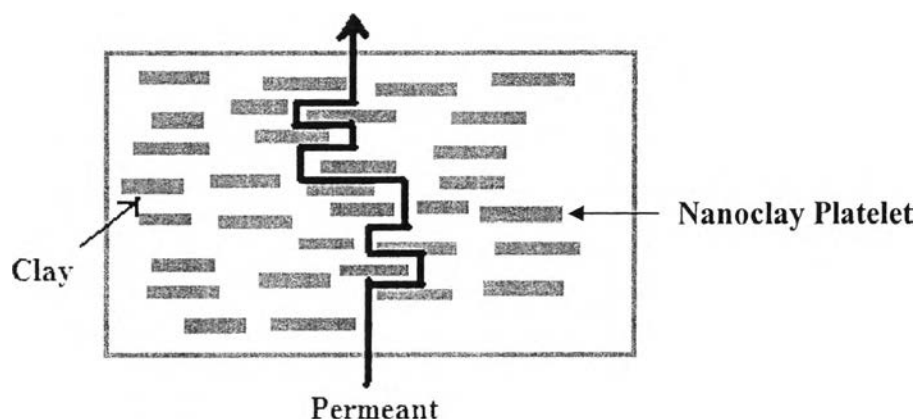
#### *2.3.5.3 Melt intercalation method*

This means has a great potential over either in situ intercalative polymerization or polymer solution intercalation thanks to its environmentally friendly method in which there is the absence of organic solvents. The method allows the use of polymers which are not appropriate for two previous modes. Moreover, it is compatible with current industrial process, such as injection and extrusion molding. Lastly, this method is concerned with annealing, statically or under shear, a mixture of the polymer and organically-modified layered silicate above the melting point of the polymer.

#### 2.3.6 Polymer-Clay Nanocomposites as Fillers in Smart Packaging

Nowadays, polymer composites are used in wide range of applications, such as transportation, construction, electronics, and consumer products. (Meneghetti and Qutubuddin, 2006)

Actually, a clay is an effective reinforcement because of its high surface area and large aspect ratio around 50-1000 (Alexandre and Dubois, 2000). Clay platelets create a tortuous path (Figure 2.7), which enhances a barrier property of packaging. (Lan, 2007). The effectiveness of clays in lessening oxygen and water permeabilities has focused on the tortuous path, which forces the gas molecule (permeant) to indirectly pass through the film. Furthermore, the nanocomposites play a crucial role in mechanical properties improvement namely increased stiffness without loss of flexibility as well as increased dimensional stability. Apart from mechanical properties enhancement, the chemical and thermal stability are increased because



**Figure 2.7** Tortuous path of a permeant in a clay nanocomposite. (adapted from Adame and Beall; Simon, 2008; Henriette, 2009)

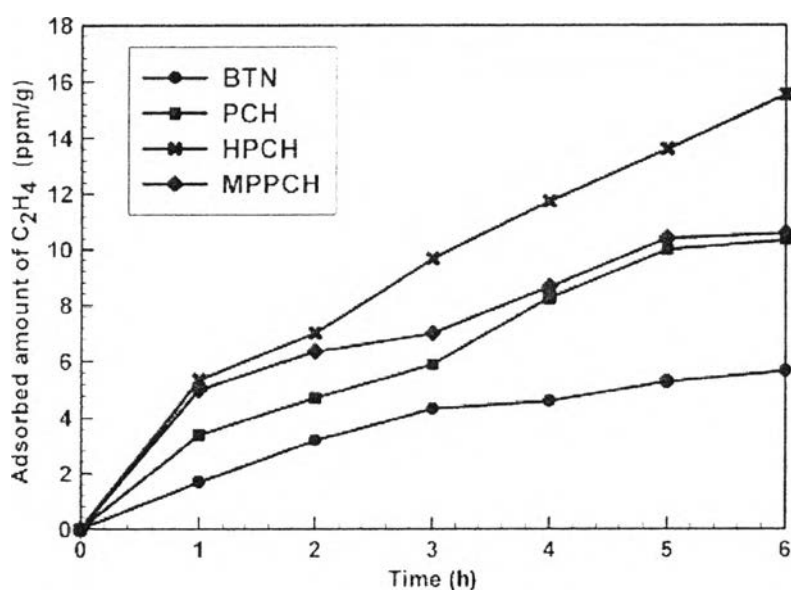
Tassanawat *et al.* (2007) conducted a research on using PP/clay nanocomposites as a pH-sensitive indicator for beverage smart packaging. The results demonstrated the occur of greater interlayer spacing of Na-BTN after being modified by cationic surfactants through ion exchange reaction. Furthermore, the organoclay added to the nanocomposites also acted as a nano-reinforcement in polymer matrix.

Ruangrit *et al.* (M.S. Thesis, 2008) carried out a research on polypropylene/organoclay nanocomposite intelligent packaging. The results pointed out that the addition of 1-5 wt.% of organoclay in the PP/organoclay nanocomposite films help enhancing thermal stability, melting and crystallization behavior. Moreover, the mechanical properties of the films showed enhanced modulus by 10 – 20 % over that of virgin PP in tensile strength and elongation at break. However, the insertion of organoclay did not affect the crystal structure of PP matrix.

Srithammaraj *et al.* (2012) conducted a research on using 3 porous materials: porous clay heterostructures (PCH) prepared by directed assembly hybridizing the surfactant and the bentonite, HPCH prepared by blending PCH and TEOS , MPPCH prepared by mixing PCH and mercaptopropyl. Afterwards, these three modified clays were further blended with PP and then blown to produce PP/clay nanocomposite films namely PCH/PP, HPCH/PP and MPPCH/PP compared to a

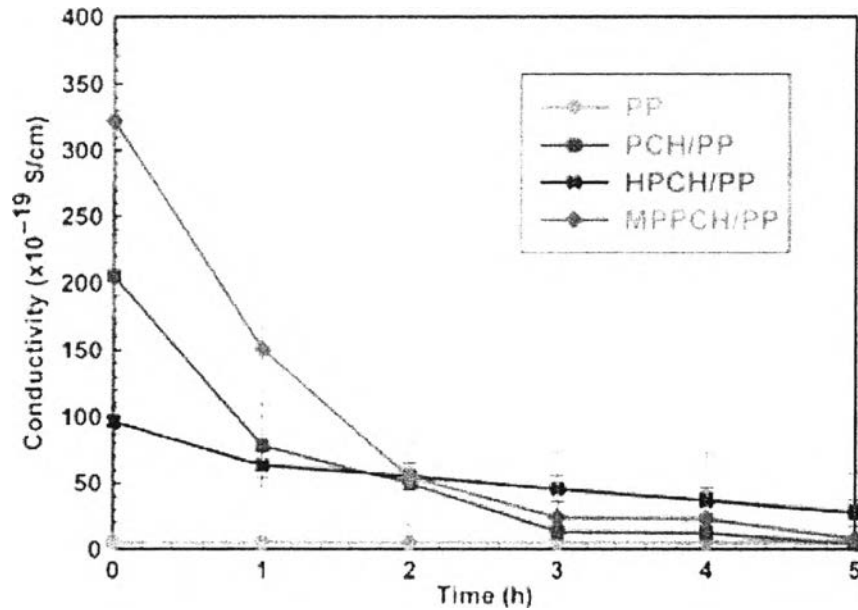
neat PP. Since they were the porous materials that could trap some gases, the material was possibly used as an ethylene scavenger in smart packaging.

The adsorption of ethylene gas (Figure 2.8) of these clays was in the order: HPCH > MPPCH > PCH > BTN based on a greater in non-polar property as a result of lower electronegativity ( $C < S < O$ ) brought about a better ethylene adsorption. Furthermore, it was also concluded that HPCH had a methyl group on the structure of pore. Hence, the similarity of the functional group between pore and the ethylene gas at the surface play a crucial role in ethylene adsorption.



**Figure 2.8** Ethylene adsorption capacity of bentonite (BTN), porous clay heterostructures (PCH) and hybrid organic-inorganic porous structures (HPCH and MPPCH).

The resulting electrical conductivity (Figure 2.9) of the film obviously showed that the largest reduction of conductivity with longer attachment time to the ethylene gas was MPPCH/PP film. This was because the film had  $-SH$  group acting as an electron acceptor, whereas the ethylene gas behaved like an electron donor at the pore area. The previously-mentioned reason contributed to the electrical conductivity reduction. This concept could be applied for the use of these materials for ethylene gas sensor.



**Figure 2.9** The Conductivity of polypropylene/clay nanocomposite films as a function of time attached to the ethylene gas.

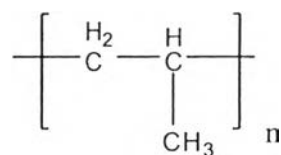
## 2.4 Overview of Polypropylene

### 2.4.1 General Description and Synthesis

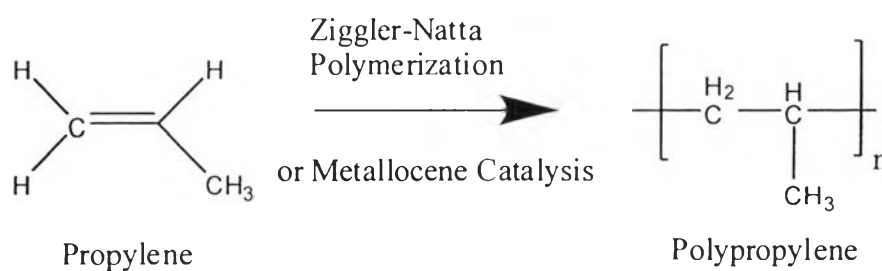
Typically, characteristics of polypropylene are stiffer and harder than PE, lower impact resistance at low temperatures in particular, high service temperatures ( $>100^{\circ}\text{C}$ ) that can be further increased with stabilization, good electric properties (insulation), does not have a tendency to stress-crack; lower chemical resistance than PE as well as better dimensional stability than PE.

### 2.4.2 Characteristic Properties

Structurally, polypropylene (Figure 2.10) is a vinyl polymer and is similar to polyethylene, Polypropylene can be synthesized from the propylene monomers by Ziegler-Natta polymerization and by metallocene catalysis polymerization (Figure 2.11).



**Figure 2.10** Chemical structure of polypropylene (PP).



**Figure 2.11** Synthesis of polypropylene.

Polypropylene (PP) is a thermoplastic for household product packaging used today (Engineering Plastic Technology – Italian Technology Consultants, <http://www.epr-italia.com>). Moreover, it is also becoming one of versatile polymers at the moment because there is wide range of applications. It is not only a plastic, but also a fiber due to serving double duty. As a plastic, it is used to make things like dishwasher-safe food containers because PP cannot be melted at temperature below 160°C (320°F). When compared to polyethylene (PE), a more common plastic, PE will anneal at about 100°C, which means that PE dishes will warp in the dishwasher. As a fiber, polypropylene is used to make indoor or outdoor carpeting, which is the kind that find around swimming pools and miniature golf courses. PP works well for outdoor carpet because PP is easily coloured and does not adsorb water like nylon. (Polymer Science Learning Center at The University of Southern Mississippi, <http://www.pslc.ws/macrog/pp.htm>)



2.4.3 Polypropylene as a Packaging Film (Spartech<sup>®</sup>, Innovative Solutions Provider, <http://www.spartech.com>)

Polypropylene is presently one of the most popular materials employed in the packaging industry. The change of its properties depends on the molecular structure chosen (homopolymer, copolymer, impact modified, etc.). During the polymerization, certain additives need using for enhancement on polypropylene film, such as anti-oxidants and nucleating agents as well as performance additives). The following list provides some general directions on advantages of PP in terms of acting as a packaging film.

#### *2.4.3.1 Advantages of Polypropylene*

- (a) Cost competitive when considering material properties such as clarity, stiffness, toughness and impact strength
- (b) Grades available to handle hot fill, and microwavable applications
- (c) Grades available that can provide high heat deflection properties that are required during retort applications
- (d) Grades available to handle frozen food to microwave applications
- (e) Environmental Stress Cracking Resistance (ESCR) properties of crystalline structure well-resising to fats and oils as well as excellent chemical resistance
- (f) Providing very good moisture barrier properties
- (g) Low taste and odor concerns. FDA (Food and Drug Administration) grades available

Tassanawat et al. (M.S. Thesis, 2007) employed PP/organoclay nanocomposites as a pH-sensitive indicator for milk packaging. They processed the PP/organoclay nanocomposites combined with indicator dyes, Bromothymol blue type- and Bromomocrysal type-films. The resulted showed that both films could response to pH changes of milk deterioration. Accordingly, PP could be blended with organoclay and then dyed with indicators in order to produce the intelligent packaging films.

Ruangrit *et al.* (M.S. Thesis, 2008) carried out a research on polypropylene/organoclay nanocomposite intelligent packaging. The result was concluded that PP was plausibly used as film packaging and demonstrated that PP/organoclay nanocomposite coated with  $\text{Cu}^{2+}$  sensor was feasibly used as an electrical-intelligent packaging for determination of meat freshness by the naked eyes at the outset of meat spoilage so-called “real-time monitoring”. Therefore, the PP/organoclay intelligent packaging film was finally obtained.

## 2.5 Roles of Silver Nanoparticles in Food Packaging

### 2.5.1 General Aspect of Silver Nanoparticles in Food Packaging

Silver nanoparticles are being immobilized in food packaging polymers intended for food packaging applications. Polymers act as carriers of silver nanoparticles. Generally, silver-based antimicrobial additives consist of metallic silver integrated into thermoplastic polymers such as polyethylene, polypropylene, polystyrene, butadiene styrene, or nylon, etc.

According to Llorens, A. *et al.* (2012), currently silver based nano-engineered materials are the most extensively used in commodities due to their antimicrobial capacity. Apart from the antimicrobial activity, they provide the enhancement on mechanical and barrier properties as well as the prevention of photodegradation of the materials. The cation migration from the packagings is the important point to consider their antimicrobial effectiveness.

The bioactivity of nano-sized silver particles (AgNPs) has been more increasing and the particles having a diameter below 100 nm exhibit optical and chemical properties that vary with particle size, shape, surface functionalization, and boundary conditions (Lloren *et al.*, 2012). Several antimicrobials are added at 0.1-5 %w/w of the packaging, especially films. Antimicrobial agents may be added by solvent-compounding technique. Processing of thermal polymers may be used with thermally-stable antimicrobial agents. For example, silver zeolites can be added as a thin co-extruded layer with other polymers at elevated temperature (up to 800°C) because silver zeolites can tolerate so high temperature (Appendini and Hotchkiss, 2002).

### 2.5.2 Types of Antimicrobial Packaging (Appendini and Hotchkiss, 2002)

Antimicrobial packaging can take several forms including:

- Addition of sachets/pads containing volatile antimicrobial agents into packages
- Incorporation of volatile and non-volatile antimicrobial agents directly into polymers
- Coating or absorbing antimicrobials onto polymer surfaces
- Immobilization of antimicrobials to polymers by ion or covalent linkages
- Use of polymers that are inherently antimicrobial

Gorup *et al.* (2011) reported a new method on synthesis of silver nanoparticles by the reduction of silver nitrate. Reducing agent was sodium citrate and stabilizer was ammonia solution. The result showed that 1.6 nm of the silver nanoparticles could be obtained and was stable approximately 18 months. Therefore, their method can be adapted for this thesis.

Shameli *et al.* (2010) synthesized the silver nanoparticles into the interlayer of montmorillonite by using sodium borohydride ( $\text{NaBH}_4$ ) as a reducing agent and chitosan as a polymer stabilizer. They noticed that the interlamellar space of montmorillonite was increased due to the as-synthesized silver nanoparticles observed by d-spacing value from an XRD. Moreover, the silver nanoparticle-montmorillonite exhibited the antimicrobial activity against Gram-negative bacteria: *E. coli* O157:H7 and *Pseudomonas aeruginosa*, and Gram-positive bacteria: *Staphylococcus aureus* and methicillin-resistant *S. aureus*.

## 2.6 **Surface modification of particulates with a silane-coupling agent**

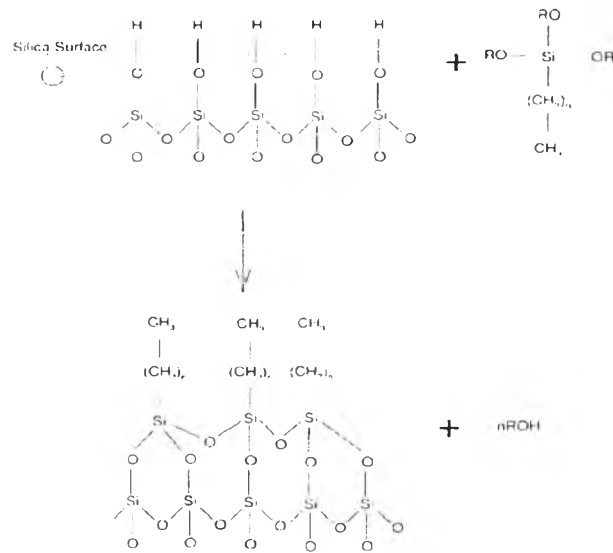
Inorganic oxide particles (i.e.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc.) are utilized as fillers in composite materials so as to enhance better mechanical, electric and magnetic as well as thermal properties. Nevertheless, these particles have to be surface-modified to increase the adhesion and compatibility between them and polymer matrices. For

example, to obtain organic-inorganic hybrid macromonomers, the surface of particles (e.g. bentonite) has to be modified by silanation, the most extensively-employed approach for surface modification, introducing 3-(trimethoxysilyl)propyl-methacrylate ( $\gamma$ -MPS) onto the surface. After finishing treating materials, reactive groups immobilized on the surface serve as free radical initiators for direct initiating the polymerization of vinyl monomers at the surface (Lin *et al.*, 2001).

Silane coupling agents are widely employed materials for improving the mechanical properties of composite materials and enhancing the stability of particles dispersion in a polymer. One of the most important factors is pH in the hydrolysis and condensation reaction of silane coupling agents in aqueous media because different agents require various processes to facilitate the effective mechanism of the agents on the surface. For instance, in case 3-glycidoxypropylmethoxysilane (GPS) needs catalyzing by both the minimum hydrolysis rate at pH 7 and the minimum condensation rate at pH 4.5 (Iijima *et al.*, 2007).

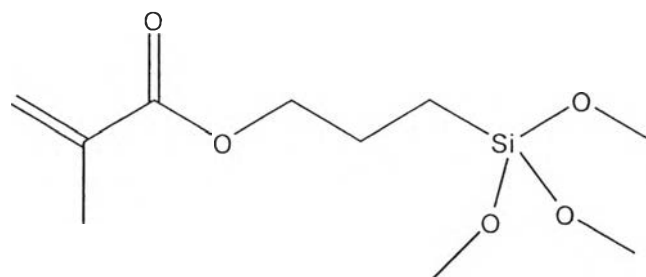
Another important factor is controlling the dispersion and the interaction of particles in the solvents. The control can help preventing the agglomeration in the surface modification and the homogeneous polymer composites can be attained as well (Iijima *et al.*, 2007).

Besides, Kim and White (2002) performed a research on the effect of different aliphatic chain length silane coupling agents on silica surface modification (Figure 2.12). The results were concluded that silane-treated silica compounds showed smaller aggregates than untreated silica compounds. Moreover, the aggregate sizes of short chain silane coupling agent-treated compounds showed meaningful reduction of aggregate sizes compared to long chain silane coupling agents. Finally, the amount of ultimate particles in one aggregates were decreased by addition of silanes.

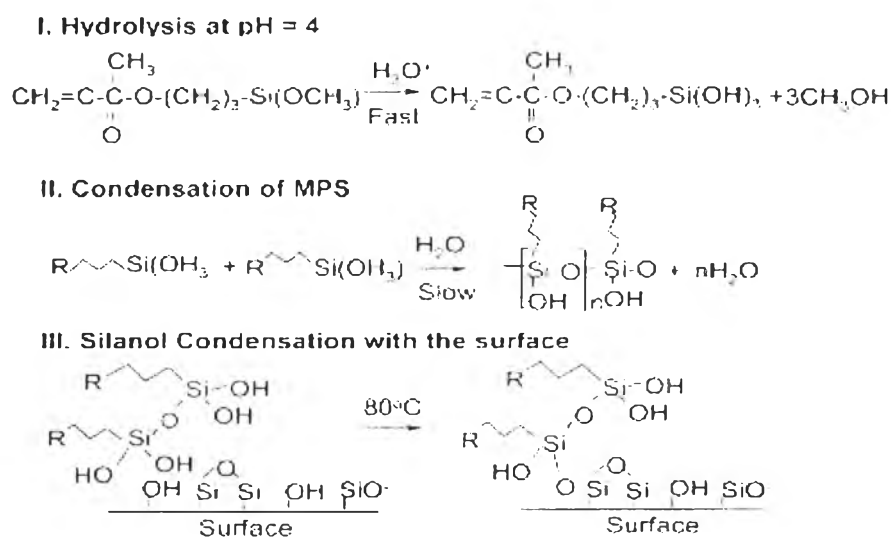


**Figure 2.12** Coupling Mechanism between Silica Surface and Silane. (Kim and White, 2002)

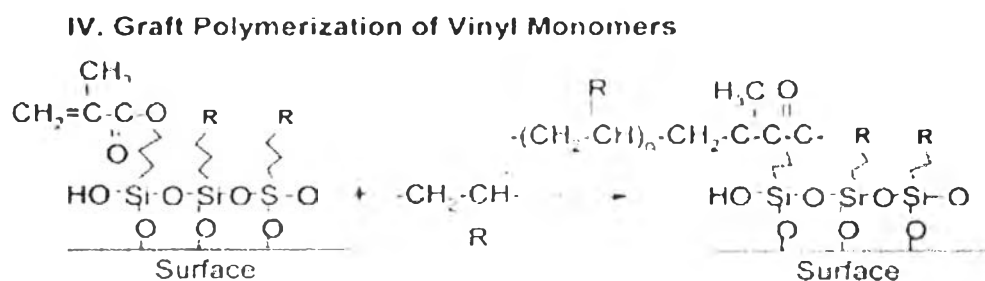
Marquez *et al.* (2005) carried out a research on surface modification of hydrophilic particulates with polymers via different methods; (1) in situ graft polymerization of vinyl monomers onto an organosilane sublayer chemically bonded to the sand surface; (2) admicellar polymerization; (3) grafting of preformed polymers onto an organosilane sublayer as well as chemically bonded to the sand surface. Regarding to my study focusing on surface modification through silanation with  $\gamma$ -MPS (Fig. 2.13) before graft polymerization of vinyl polymers, sand particles were firstly washed before silanation. After completing the silanation process with  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS) as following (Fig. 2.14), a silane of the particles were grafted with vinyl monomers via different approaches (Fig. 2.15). The vinyl polymers used in their graft polymerization were acrylamide, acrylic acid and vinyl acetate, polymer isolation, and preformed water-soluble polymers.



**Figure 2.13** The chemical structure of  $\gamma$ -MPS.



**Figure 2.14** Schematic illustration of surface modification via the silanation with  $\gamma$ -MPS. (Marquez *et al.*, 2005)



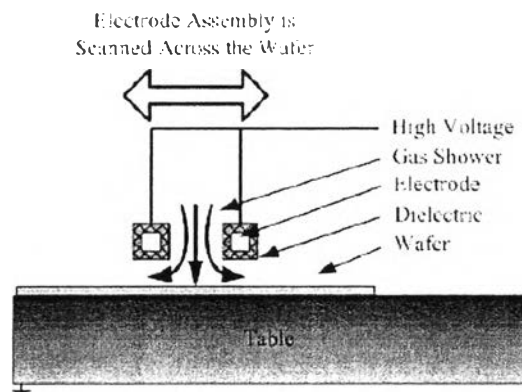
**Figure 2.15** Schematic representation of graft polymerization of vinyl monomers onto a silane layer. (Marquez *et al.*, 2005)

The sand surface after treatment was characterized by Raman Spectroscopy and the amount of material covering the surface was determined by gravimetric analysis as well as contact angle measurement of the samples. The results clearly showed that there are characteristic peaks of organosilane (MPS) consistent with the mechanism of adhesion via silane-coupling agents shown in figure 13. In order to find the optimum condition for graft polymerization of monomers onto the surface, polymerization conditions were determined by means of gravimetric analysis. The results point out that the in situ graft polymerization of vinyl monomers rendered the low grafting densities. In my research, dielectric barrier discharge (DBD) plasma technique is chosen in order to increase grafting densities by inducing free radicals onto the silane layers of particulates (silane-modified sodium bentonite) for further graft polymerization of vinyl polymer (polypropylene) so that the PP/nanocomposites will be obtained in form of exfoliated clay confirmed by XRD.

## **2.7 Potential Use of Plasma Technology**

Plasma is the fourth state of matter. It is a gaseous mixture of free electrons and ions that have a high mean kinetic energy, so the charge carriers affect each other because of their inherent charges and energies, as well as are also influenced by external fields (Panicker, M.S. Thesis 2003)

Presently, in several industries plasma is utilized in a variety of services, such as medical products and semiconductors, in lighting and lasers, welding technology, etc. The potential application for the generation of plasma in this study is the manufacturing of polymer-clay nanocomposites for a smart packaging.

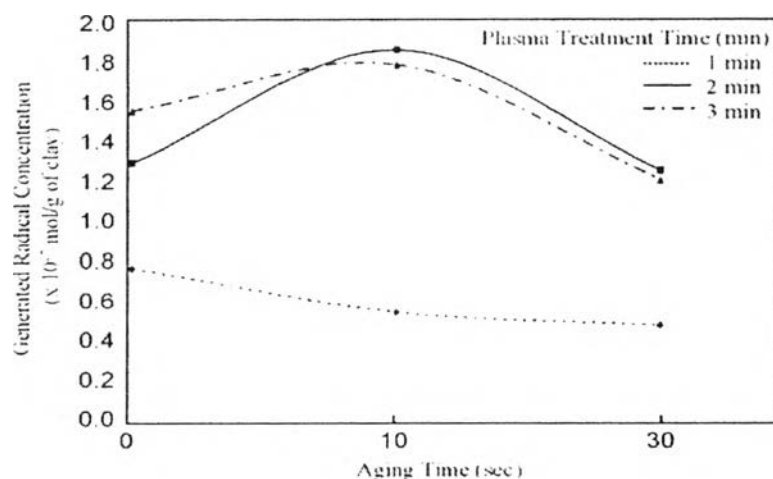


**Figure 2.16** Schematic representation of plasma generator. (Galchev *et al.*, 2007)

Such a plasma discharge (Figure 2.16) renders mechanically non-destructive, chemically-mild and friendly ways of altering free radical generation. Moreover, the plasma process succeeds in effectively-accomplish modification of the topmost region without having an effect on the desirable bulk properties of a polymer. (Tasanatanachai *et al.*, M.S. Thesis, 2008)

Tasanatachai and Magaraphan (2008) performed a research on using air plasma operated at atmospheric pressure and 23 kV voltage fixed were applied for treating clay before grafting with styrene monomer by varying two parameters, treatment time and aging time, which affected plasma system. The result (Figure 2.17) demonstrated that 2 min treatment-time and 10 sec aging-time were the optimum condition for the plasma process, which rendered the maximum of generated radical concentration around  $1.8 \times 10^{-7}$  mol/g of clay. Besides, the result showed that after grafting with polystyrene (PS), the nanocomposites were greater impact strength than pure polystyrene (PS) seeing that the plasma could be used to improve interfacial adhesion between clay and polymer matrix.





**Figure 2.17** Effect of aging time on total radical concentration generated on surface of clay with various plasma-treatment time using 23 kV applied voltage.

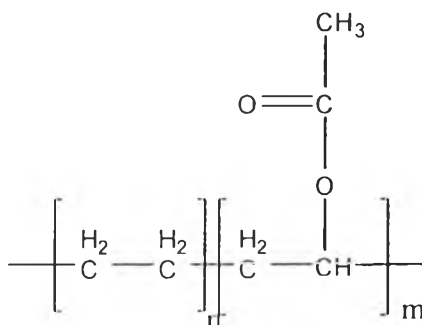
Concerning a gas used in the plasma process, there are various categorizes of carrier gases. The gaseous plasma can modified the surface with the induction of both nitrogen and mainly oxygen based functional groups (Tasanathanachai *et al.*, M.S. Thesis, 2008). In the thesis, the plasma treatment of sodium bentonite is operated at atmospheric pressure under air by varying two parameters affecting the plasma system, plasma-treatment time and aging or storage time in order to investigate the optimum condition for plasma treatment.

## 2.8 Overview of Ethylene-Vinyl Acetate Copolymer (EVA) (Henkel, 2011)

### 2.8.1 General Description

Ethylene-Vinyl Acetate Copolymer (Figure 2.18) is the copolymer of ethylene and vinyl acetate (<http://www.foodnetworksolution.com>), which is formed via continuous bulk polymerization or solution polymerization. The solution polymerization is predominantly used because the bulk polymerization generates polymer which is too low molecular weight to be useful in the rubber industry. Ordinary grades have vinyl acetate contents ranging from 2% to 50% but the crystallinity decreases from 60% to 10%, respectively. It is concluded that the more

vinyl acetate content, the less amount of the crystallinity of the polymer. The EVA can be not only a thermoplastic elastomer, which is able to be processed by common methods such as extrusion, injection molding, blow molding, calendaring, and rotational molding, but a thermoset rubber resulting from subsequent cross-linking with a peroxide cure system as well.



**Figure 2.18** The chemical structure of ethylene vinyl acetate (EVA).

### 2.8.2 General Properties

EVA is an extremely elastic material that is able to form a porous material similar to rubber but with excellent toughness. It is three times as flexible as low-density polyethylene (LDPE), which exhibits tensile elongation of 750% with a peak melting temperature of 250°F (96°C). The material has good barrier properties, low-temperature toughness, stress-crack resistance, hot-melt adhesive, waterproof properties, and resistance to ultraviolet radiation. Indeed, EVA has little or no odor and is competitive with rubber and vinyl products in many electrical applications. In sum, the key benefits of its properties are soft and extremely elastic still tough, good clarity and gloss with little or no odor as well as competitive with rubber and vinyl in many electrical applications (<http://www.porex.com>).

In fact, the properties of EVA copolymer primarily depend on the amount of vinyl acetate in the copolymer. At low content of vinyl acetate, the copolymer is a thermoplastic similar to properties of low density polyethylene (LDPE). While vinyl acetate content is increased, the copolymer takes on the performance characteristics of a thermoplastic elastomer until the crystallinity drops so low that the copolymer forms a soft rubbery material with minimal physical strength. The copolymer containing high vinyl acetate content is primarily used as a component in adhesives

and coatings but can be vulcanized to obtain useful physical properties. As the solubility in organic solvents and clarity increases with increasing levels of vinyl acetate. The lowered crystallinity caused by the addition of the vinyl acetate leads to good durability at lower temperatures and environment stress cracking resistance. The enhanced flexibility is accompanied by lower softening point temperatures as the level of vinyl acetate increases, which limits the upper service temperatures of these materials. EVA has good resistance to salt water and bases. However, it is not miscible with strong oxidizers. Grades offering good resistance to hydrocarbon greases are available, yet general speaking, copolymers are readily soluble in a wide range of aliphatic, aromatic and chlorinated solvents. Furthermore, grades offering good resistance to UV degradation and ozone are available as well (Table 2.5).

**Table 2.5** Typical applications of EVA.

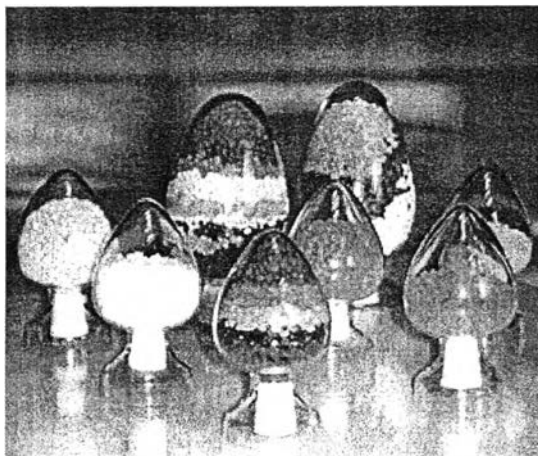
<b>Applications</b>	<b>Illustrations</b>
Appliances	Freezer door gaskets, Convolutud tube for vacuum cleaners
Electrical	Foams for static sensitive devices
Industrial	Hoses, Tubes
Packaging	Shrink wrap film
Medical	Disposable gloves, Anaesthesia face masks and hoses
Miscellaneous	Adhesives, Coating, Sealants, Solar cell encapsulants, Baby bottle nipples

### 2.8.3 Advantages of EVA Copolymer

The EVA has many advantages which are fast-fixturing, high adhesion to plastics, wide variety of formulations available, and low volumetric cost. Additionally, the EVA is a hot melt additive, which is one-part and solvent-free thermoplastic adhesives that are solid at room temperature and a low to medium viscosity (750 – 10,000 cP) adhesive at dispense temperatures (typically greater than 195°C). The EVA can be rapidly cooled to form a strong bond after dispensing. At the cured or cooled state, the EVA melt can be varied in physical properties from soft rubbery and so tacky to hard and more rigid. In addition, the melt also has excellent long-term durability and resistance to moisture, chemicals, oils, and temperature shocks. EVA hot melts are the “original” hot melt and are considered as the low cost and low performance hot melt. To illustrate, EVA provides a good adhesion to steel aluminum, rubber, and various plastics, typically including box and carton sealing. EVA hot melts are also capable of being formulated to carry a Food and Drug Administration (FDA) approval for use in food packaging. Out of all available hot melts, EVA generally has the poorest high-temperature resistance. EVAs available in the market at the moment are Elvax<sup>®</sup>, Escorne<sup>®</sup>, Evazote<sup>®</sup>, Ultrathene<sup>®</sup> from DuPont<sup>™</sup>, Exxon Chemical<sup>™</sup>, B.P. Chemicals<sup>™</sup> and Quantum Chemicals<sup>™</sup>, respectively.

### 2.8.4 EVA color masterbatches (<http://www.chinamasterbatches.com>)

EVA has competence in being colored by various pigments. EVA colored masterbatch (Figure 2.19) is the best alternative material for EVA foaming products, such as EVA slipper, shoes soles, tires, pads, EVA toys and swimming board, etc.



**Figure 2.19** Colored EVA masterbatch. (<http://www.chinamasterbatches.com>)

Naneraksa and Magaraphan (2011) produced an intelligent film prepared by the first combination of 4 wt.% natural dye from mangosteen pericarp and ethylene vinyl acetate (EVA) by melt blending and secondly, compressed it in form of film. The performance of pH-indicator film could be sensitive to the change in pH. The color change based on CIELAB system was characterized. The result showed that the color was able to gradually change in response to change in pH as a result of anthocyanin and  $\text{NH}_3$  gas during the spoilage of chilled-fresh fish in film packaging.

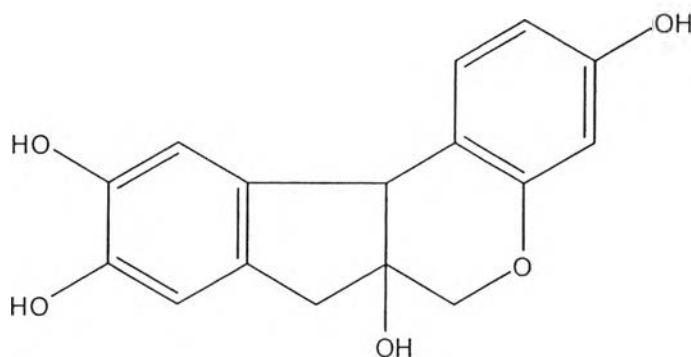
## 2.9 Natural Dye from Sappan Wood)

In response to food safety concern, natural dyes are deliberately chosen as pH-sensing film in order to monitor the fish spoilage.

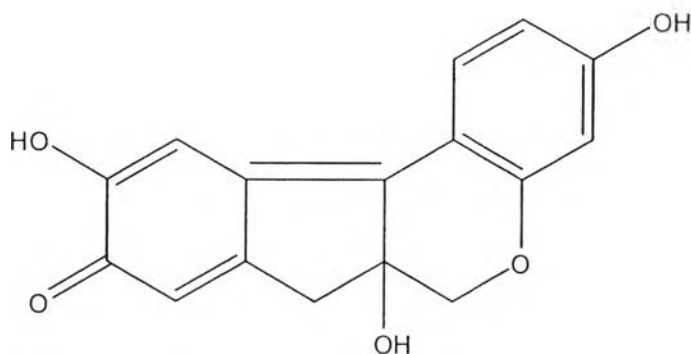
### 2.9.1 Sappan Heartwood (Rattanapatipan and Patanathabutr, 2009)

Sappan wood or Indian red (*Caesalpinia sappan* L.) is an indecious tree widely planted in Thailand. Its heartwood has been used as traditionally oriental medicine in order to treat infectious diseases long time ago. Moreover, the color extractant is able to be used to dye cotton and silk for a red-shade yarn. The dye molecule in sappan heartwood is an oxidized form of brazilin (Figure 2.20) or so-called brazilein (Figure 2.21). Brazilein has a chromophore absorbing light in the wavelength between 400 – 500 nm, so it shows the complementary color to eyes as a

red shade. For acid condition, the absorption wavelength of the chromophore is in the range between 480 – 490 nm and shows an orange shade, while in alkaline atmosphere, the absorption wavelength ranged from 500 – 560 nm and shows a purple shade.



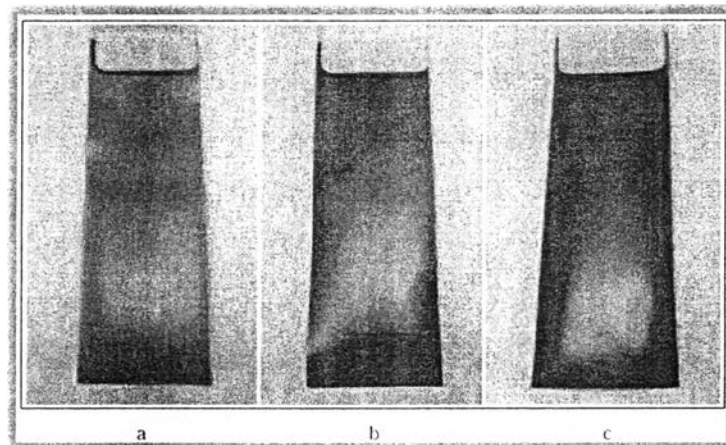
**Figure 2.20** The chemical structure of brazilin.



**Figure 2.21** The chemical structure of brazilein.

Rattanapatiphan, S. (2009) carried out a research on natural dye-aluminium-silicate polymer composites for pH indicator by preparing the composites of a color from sappan wood (*Caesalpinia sappan* L.) extractant, polyvinyl alcohol (PVA) and aluminium-silicate via sol-gel technique with different emulsifiers as anionic surfactant and ethanol. The results (Figure 2.22) pointed out that the pH-sensing composites films was capable of showing visual changes in colors to acid and

alkaline atmospheres, so the color can be applied as acid-alkaline indicators in food packaging.



**Figure 2.22** The visual change of PVA-sappan dye films in (a) acidic, (b) neutral, and (c) basic conditions.

Above all, the color from sappan heartwood is likely to be used as part of intelligent section of smart packaging in the research. Therefore, it is evident that the natural dye colors can be used as a pH sensor for monitoring spoilage of agricultural products instead of commercially synthetic dyes that probably have a detriment impact on human health.

## 2.10 Colorimetric Measurement based on CIELAB System

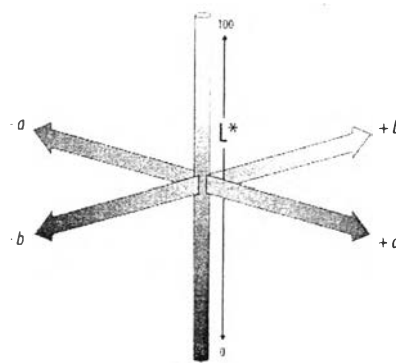
### 2.10.1 Background of CIELAB system

The CIELAB color system recommended by CIE (Commission Internationale de l'Éclairage) is usually referred to the CIELAB system (University of Johannesburg, [www.uj.ac.za](http://www.uj.ac.za))

The CIE  $L^*a^*b^*$  system offers the following important concepts ([www.datacolor.com](http://www.datacolor.com)):

- a. It is perceptually uniform.
- b. It is based on the useful and accepted theory of opponent colors.

The CIE  $L^*a^*b^*$  Color Scale is an approximately uniform color scale in which the differences between points plotted in the color space corresponding to visual differences between colors plotted. The CIELAB color space is organized in a cube form. The  $L^*$  axis runs from top to bottom, so the maximum  $L^*$  is 100 which represents a perfect reflecting diffuser (white) and the minimum  $L^*$  is 0 which represents black. The  $a^*$  and  $b^*$  axes do not have specific numerical limits. Positive  $a^*$  is red and the negative one is green. Positive  $b^*$  is yellow and the negative one is blue. A diagram (figure 24) representing the CIELAB color space is shown as following.



**Figure 2.23** The diagram representing the CIELAB color space. (School of Medicine, University of South Calorina)

#### 2.10.2 Colorimetric Method based on CIELAB Color System

In the color measurement field, it is necessary to not only assess the data obtained from the CIELAB system, but also compare the color of objects to one another. The colorimetric calculation formula of CIE ( $L^*$ ,  $a^*$ ,  $b^*$ ) was set up in 1976. The colorimetric value is expressed as  $\Delta E$  (total color difference, TOC); “ $\Delta$ ” means discrepancy whilst “ $E$ ” from the first letter of the word “*Empfindung*”, which means “feeling”, is calculated as below equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (\text{Eq. 2.1})$$



where  $\Delta L^*$  being the lightness difference,  
 $\Delta a^*$  being the red/green difference,  
 and  $\Delta b^*$  being the yellow/blue difference.

The values of  $L^*$ ,  $a^*$ , and  $b^*$  are the CIELAB color system axis, which are measured by using a commercial color scanner. Table 2.6 shows the relationship between  $\Delta E$  value and visual assessment.

**Table 2.6** Relationship between  $\Delta E$  value and visual assessment (color difference) (University of Johannesburg)

$\Delta E$	Color Difference
Up to 0.2	Not visible
0.2 – 0.5	Very slight
0.5 – 1.5	Slight
1.5 – 3.0	Obvious
3.0 – 6.0	Very obvious
6.0 -12.0	Large
More than 12.0	Much large

From the Table 2.5, it is vividly noticed that the more  $\Delta E$  value, the more obvious color difference of sample, which can be detected by the naked eyes.

### 2.10.3 Advantages of Colorimetric Method by CIELAB Color System

CIE  $L^*a^*b^*$  colorimetric method is the main method accepted and widely used for measuring color worldwide. There are three important advantages:

- a. Calculations are simple and a small model computer can be used to do this work.
- b. The anticipated results will be similar to those generated by applying the formula.
- c. The system is easily understood and it is able to be used by people who have no background on this color system.

From the above reasons, the colorimetric technique is the main color detection method employed in this research and it is already widely used in the precast industry.

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