CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Intelligent or Smart Packaging

Intelligent packaging is defined as packaging systems that monitor the condition of food to provide information on the quality of the packaged food during transport and storage. A variety of indicators that belong to the group of intelligent system are of interest to the food-packaging chain, such as indicators of temperature, time-temperature, pack integrity, microbial growth, product authenticity and physical shock. Many indicator system have been patented, especially temperature and time-temperature indicators. Only a limited number of these patents have been commercialized because of strict requirement: an indicator must be easily activated, exhibit an easily measurable, reproducible time/temperature-dependent change, be irreversible, and ideally correspond or easily be correlated to food quality. Commercially available indicators of interest for monitoring the food quality include indicators of time-temperature, leakage and freshness (Kruijf *et al.*, 2002).

The definition of intelligent packaging in the Actipak project (Ahvenainen *et al.*, 2003) includes indicators to be used for quality control of packed food (Table 2.1). They can be so-called **external indicators**, i.e., indicators which are attached outside the package (time-temperature indicators), and so-called **internal indicators** which can placed inside the package, either to the head-space of the package or attached into the lid (oxygen indicators for indication of oxygen or package leak, carbon dioxide indicators, microbial growth indicators and pathogen indicators).

Table 2.1 Examples of external and internal indicators and their working principle or reacting compounds to be used in intelligent packaging for quality control of packed food (Ahvenainen *et al.*, 2003)

Indicator	Principle/reagents	Give information about	Application
Time-temperature indicators (external)	Mechanical Chemical Enzymatic	Storage conditions	Foods stored under chilled and frozen conditions
Oxygen indicators (internal)	Redox dyes pH dyes Enzymes	Storage conditions Package leak	Foods stored in packages with reduce oxygen concentration
Carbon dioxide indicators (internal) packaging	Chemical	Storage conditions Package leak	Modified or controlled atmosphere food
Microbial growth indicators (internal/external) i.e. freshness indicators	pH dyes All dyes reacting with certain metabolites (volatiles or non volatiles)	Microbial quality of food (i.e. spoilage)	Perishable foods such as meat, fish and poultry
Pathogen indicators (internal)	Various chemical and immunochemical methods reacting with toxins	Specific pathogenic bacteria such as *Escherichia coli* 0157	Perishable foods such as meat, fish and poultry

2.2 Freshness Indicators

Freshness indicators is an ideal indicator for the quality control of packaged food stuffs would indicate the spoilage or lack of freshness of the product, in addition to temperature abuse or package leaks (Figure 2.1) (Kruijf *et al.*, 2002). Freshness indicators attached inside the package indicate directly the microbiological quality of the product. The indication is based on a reaction between the indicator and the (volatile) metabolites produced during growth of micro-organisms in the product. A

variety of different systems for freshness indicators have been presented in the litera-
ture and patents. For example, a system for hydrogen sulphide as a freshness indica-
tor for poultry products has been developed. However, there is only a limited number
of commercially available freshness-indicating systems, one of which is an indicator
label reacting to volatile amines from fish with a visual color change. Other indicator
systems have been proposed, e.g., for CO_2, diacetyl, and ammonia (Hurm E., 2002).
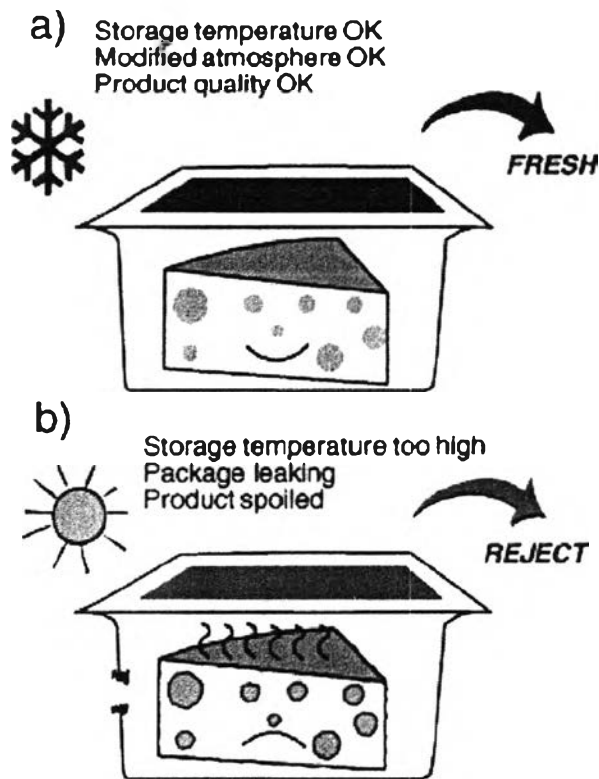
Figure 2.1 Freshness indicator which gives information on the spoilage or lack of
freshness of the product, in addition to temperature abuse or package leaks (Hurm E.,
2002).

2.3 Fish Freshness

Fresh fish are one of the most perishable of all foods. The rate of spoilage
rise with temperature. They must be refrigerated or frozen immediately after harvest
and kept refrigerated until eaten. Any departure from immediately and continued re-

frigeration will lead to flavor and texture losses. If the fish are of poor quality to start with, the quality loss will be even more pronounced.

Spoilage of fish is not clearly defined. Obvious signs of spoilage are formations of off-odors and off-flavors, slime formation, gas production and changes in texture. The development of these spoilage conditions in fish and fish products is due to a combination of microbiological, chemical and autolytic phenomena. **Autolytic spoilage** is responsible for the initial loss of quality in fresh fish, but contributes very little to spoilage of chilled fish and fish products. The decomposition of the fish occurs as its constituent compounds break down. The proteins, nucleotides and sugars break down, bases are released, the pH falls and the fats are oxidised. These make the fish smelly, rancid and tough. The physical, chemical, and bacteriological characteristics of fish vary with species, seasons, methods of capture, fishing grounds etc. However, it is possible to describe the changes that take place after death, until the fish is totally spoiled and unfit for human consumption. The changes in fish have three main groups of causes: bacteria, digestive enzymes and others (e.g. oxidation leading to rancidity) (Baixas-nogueras *et al.*, 2002).

2.3.1 Methods to Evaluate Freshness

Numerous methods may be used to evaluate freshness of fish. In general the main practical methods of determining fish freshness quality involve sensory evaluation, chemical analysis, physical instruments and microbiological methods.

2.3.1.1 Sensory Methods

Sensory methods based on changes in its appearance, odor, color, flavor, and texture. Speed, simplicity, and low cost are the main advantages of these methods. However, sensory analyses are inherently subjective, even when panel members have received extensive training. For this reason, chemical methods have been developed to measure the amounts of breakdown products derived from either bacterial or endogenous enzymatic activity. In particular, chemical parameters, such as volatile and nonvolatile amine levels, have been used to assess fish freshness.

2.3.1.2 Chemical Methods

Chemical methods of measuring freshness quality are considered to be objective and consequently superior to methods involving sensory

evaluation. Odor is one of the most important parameters to evaluate fish freshness. During storage of fish the odor undergoes changes, from fresh odor, sweet and stale odors until the final phase of spoiled or putrid odors. Volatile compounds contributing to odor changes can be measured to evaluate the freshness and spoilage of fish. During the deterioration of fish amines are formed. One of the chemical methods makes use of the total volatile basic compounds (TVB) in fish, which contains mainly ammonia, trimethylamine (TMA) and dimethylamine (DMA), the levels of which increase with spoilage by either bacterial or enzymic degradation (Milanes M., 2004). The measurements of total volatile basic nitrogen (TVB-N) have been used in the fish industry as an indicator of quality for fish and fish products. In fact, there is an European Union regulation that considers a TVB-N value of 30-35 mg/100 g as the limit above which fish is not acceptable for human consumption (Baixas-nogueras *et al.*, 2002).

2.3.1.3   Physical Methods

Physical methods have also been used to evaluate fish freshness. These include measurements of time-temperature indicators (TTI), mechanical, microstructure, electrical properties, color measurements, spectroscopy and pH.

2.3.1.4   Microbiological Methods

Microbiological methods have been used to evaluate the possible presence of bacteria of public health significance. The number of specific spoilage bacteria will give information on the remaining shelf life which can be predicted from such numbers. Microbial measurements can be used to evaluate the degree of fish freshness. When such microbiological measurements are needed it is recommended to use the numbers of specific spoilage organisms (SSO) or classical total viable counts (TVC) measurements (Milanes M., 2004). A clear distinction should be made between the terms spoilage association and spoilage organisms (bacteria) since the first describes merely the bacteria present on the fish when it spoils whereas the latter is the specific group that produces the off-odors and off-flavors associated with spoilage (Figure 2.2). When stored aerobically, levels of 10^8-10^9 cfu/g of specific spoilage bacteria are required to cause spoilage of fish (Gram L. and Huss H., 1996).
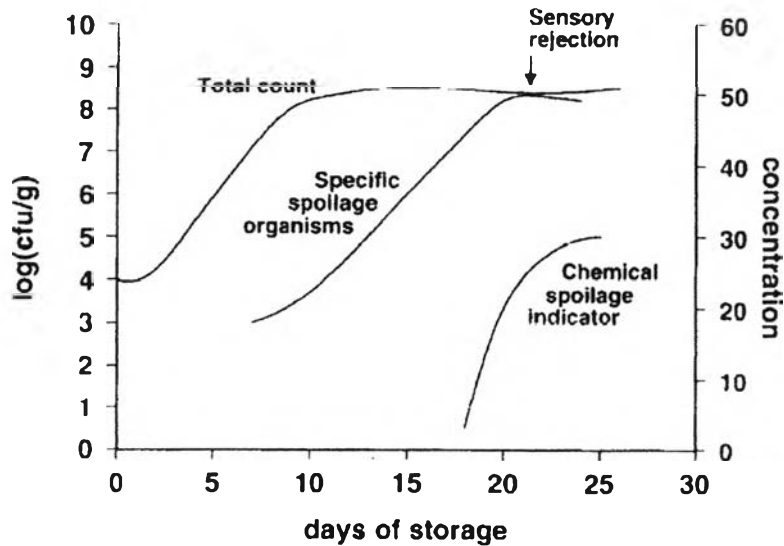
Figure 2.2 Model of changes in total count (TVC), specific spoilage organisms (SSO) and chemical spoilage indices during chill storage of a fish product.

2.4 The Use of Freshness Indicators in Fish Packaging

The intelligent or smart packaging monitors and gives information about the quality of the packed food. The changes taking place in the fresh food product can be categorized as (i) microbiological growth and metabolism resulting in pH change, formation of toxic compound, off-odor, gas and slime formation, (ii) oxidation of lipids with adverse biological reactions or discoloration (Ahvenainen *et al.*, 2003).

The focus of this research is on intelligent concept indicating the changes mainly belonging to the first category. The package which incorporated with freshness indicator base on the use of pH dyes can inform the spoilage of fish by color change of indicator due to the presence of microbial metabolites produced.

Furthermore, the fish industry and retailers are interested in methods that are objective, cost effective, rapid, reliable and non-destructive. Various approaches have therefore been used for the determination of fish quality. Typical methods include sensory (odor, taste, and texture), microbiological (total viable count or TVC), physical (texture, and electrical properties) and chemical (K and K_1 values, Total Volatile Basic Nitrogen or TVB-N, lipid oxidation). Pacquit *et al,.* (2006) had devel-

oped an inexpensive "chemical bar-code", in the form of on-package sensor spots that monitored spoilage in fish products. A solid-state sensor based on pH sensitive dye, bromocresol green, that indicated by a visible color change (yellow to blue) the presence of volatile spoilage compounds such as trimethylamine (TMA), ammonia (NH_3) and dimethylamine (DMA) collectively knew as TVB-N. The sensor characteristics were studied as well as its response with standard ammonia gas. The approach was sensitive to volatile amines, with a linear response to ammonia gas concentration from 0 to 15 ppm (Figure 2.3).
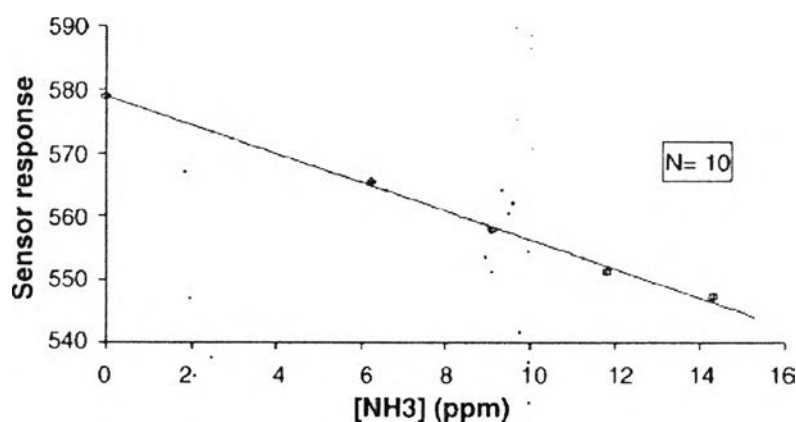
Figure 2.3 Sensor responses (spin-coated at 1000 rpm) to ammonia concentration monitored by the optical scanner.

Trials on cod, whiting and under-utilised species (Roundnose brigadier and Cardinal) enabled real time monitoring of their spoilage and the sensor responses were found to correlate to the changing of microbial populations (TVC and *pseudomonas* in tissue) in fish samples. The sensor response could be integrated with a simple, inexpensive reflectance colorimeter that they had developed based on two light emitting diodes (LEDs) and a photodetector. The results showed clearly that not only did the sensor response correlate with the changes in both bacterial populations but the onset of sensor color change also correlates with the level of product rejection (10^7 cfu/g) for fresh fish samples to reach end of shelf life. These levels were reached after about 18 h in their experiments (Figure 2.4). A delay between the rise in microbial population and the sensor response curves was also apparent from Figure 2.4.

This delay was inherent as volatile base generation follows the increase in SSO population. Thus, the sensors accurately tracked the increase in volatile base concentration in the package headspace and since the region of change in sensor color coincides with higher levels of SSO in the fish tissue, the scanner measurements of on-package sensor color were useful indicators of approximate SSO population and therefore spoilage of the fish samples. It was however important to mention that since the observed color change always lags behind the rise in microbial population, this also means that it would not precede it and those false positive results could not occur.
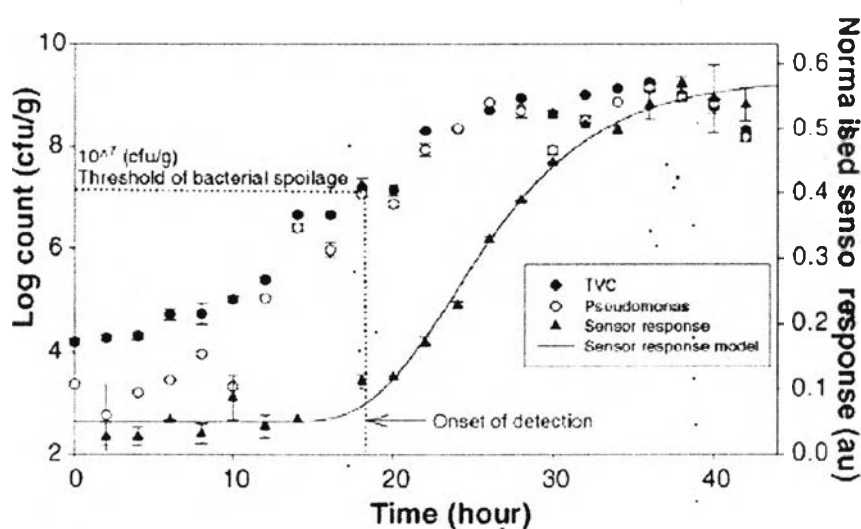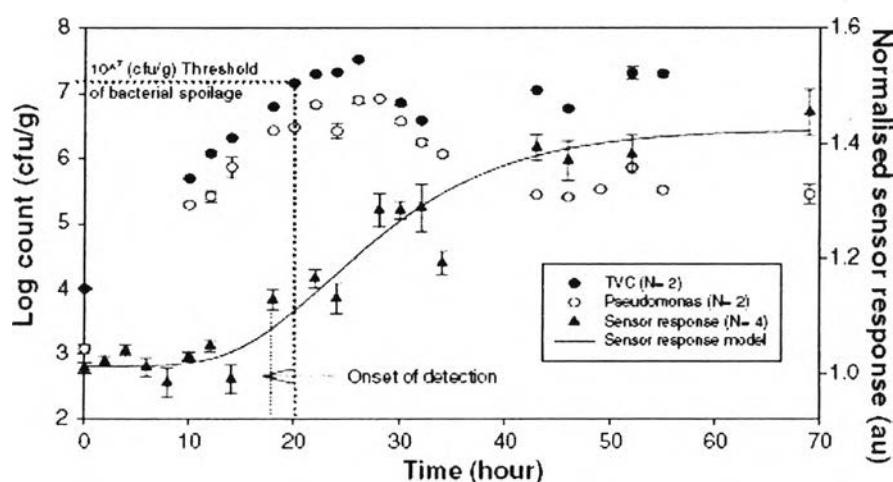

Figure 2.4 Correlation of sensor response (1000 rpm) and changes in bacterial population of fresh cod kept at 20°C over time.

Recently, Pacquit *et al,.* (2006) described the fabrication and application of a "smart packaging" that monitored the microbial breakdown products in the headspace of packaged fish. When a fish spoiled it release a variety of basic volatile amines which were detectable with appropriate pH indicating sensors. These were prepared by entrapping within a polymer matrix a pH sensitive dye that responds, through visible color changes to the spoilage volatile compounds that contributed to a quantity knew as total volatile basic nitrogen (TVB-N). Bromocresol green (pKa 4.72) has a well-defined color change from yellow to blue (which was easily visible by eye) and was suitable to use in the pH range of interest. Two fish species (cod and

whiting) were selected for investigation. Laboratory trials on fresh fish filets showed that the sensor accurately tracks the increase in amines concentration in the package headspace. The response was also found to correlate to changing microbial populations (total viable count or TVC and *Pseudomonas spp.*). In addition, leaching of the dye was assessed over time to assess the suitability of the sensor formulation for food packaging application. Tetraoctyl ammonium bromide reduced leaching by 82% and was selected for the fish spoilage trial. The sensor response was found to correlate with bacterial growth patterns in cod and whiting fish samples thus enabling the "real-time" monitoring of spoilage. The result showed that the TVC counts were found to slowly increasing from approximately 10^4 cfu/g during the initial 10 h but sharply rising from then on, reaching values of 10^7 cfu/g at approximately 18 h before stabilizing at 26 h just above 10^7 cfu/g (Figure 2.5). Clearly, this coincides with the onset of color change in the sensors (14–24 h) suggesting that the concentration of spoilage compounds in the headspace had reached the sensor lower detection limit. Thus, the sensors accurately track this increase in volatile base concentration in the package headspace. The region of change in sensor color coincides with higher levels of *Pseudomonas spp.* in the fish tissue. Therefore, the scanner measurements of on-package sensor color were useful indicators of *Pseudomonas spp.* population and therefore spoilage of the fish samples.

Figure 2.5 Normalised data showing the correlation between sensor response and bacterial population (TVC and Pseudomonas spp.) in cod filet samples at 21°C. The error bars are SEM (standard error of the mean) values.

Moreover, Hong *et al,.* (2000) studied the use of color indicators as an active packaging system for evaluating kimchi fermentation. Kimchi fermentation was assessed for titratable acidity (TA), and color changes of the indicators were measured and expressed as Hunter values as well as total color difference (TCD). TCD values of bromocresol purple (BP) type indicator (containing BP as a chemical dye) ranged 27±33 and were much more than those of methyl red (MR) type (containing MR). The developed color indicator film consisted of polypropylene (PP) resin, calcium hydroxide as a CO_2 absorbent, and bromocresol purple (BP) or methyl red (MR) as a chemical dye. Changes in Hunter color values of the indicators within the packages of kimchi. In case of the indicator containing BP, Hunter L and b values increased gradually with storage time, while Hunter a value decreased slowly and then remain constant. However, Hunter L and b values of the indicator containing MR decreased exponentially, while Hunter a value increased remarkably and remained constant. The result meant that color of the BP type indicator turned from initially blue to finally light green, and that of the MR type turned from light orange to red. The rate of the color changes was different depending on temperature but with the same pattern. Present results suggest that the BP type indicator could be used successfully as a full time-fermentation indicator for kimchi products. However, the MR type might be applied only as a ripeness/unripeness indicator to packaged kimchi because its color change rate nearly reached to zero at the TA values more than 0.7 mg/dl.

Two years later, Hong *et al.* developed kimchi packaging by using gravure-printed color indicators on common nylon/polyethylene (Ny/PE) film. A gravure process was successfully applied as a novel approach to fabricate color indicators for kimchi packaging. The color changes of the developed indicators properly represented the degree of fermentation of packaged kimchi. These color indicators could be employed as an effective intelligent packaging technology for monitoring ripeness of kimchi products non-destructively.

As mentioned before, among various applications of the nanocomposites, intelligent system as a new food-packaging systems have been developed. The dispersed clay mineral takes many beneficial roles in the term of intelligent system and supporting by these reviews, the incorporation of indicator dye, such as bromocresol

green into PP/clay nanocomposite could be developed to be smart packaging to evaluate fish spoilage. Therefore, it will be concerned and studied in this thesis work.

Those are the literature reviews about indicator dyes incorporated polymer used as a smart packaging. In this work, the organoclay nanocomposite as a nano reinforcement in polymer matrix was also interested due to thermal and mechanical property improvements of polymer.

2.5 Surface Modification of Clays

One of the drawbacks of clays is the incompatibility between hydrophilic clay and hydrophobic polymer, which often causes agglomeration of clay mineral in the polymer matrix. Therefore, surface modification of clay minerals is the most important step to achieve polymer nanocomposites. The modification of clay polarity to provide the organophilic character to the clay is the requirement for successful formation of polymer-clay nanocomposites. Organophilic clay can be formed from normally hydrophilic clay by means of an ion exchange with an organic cation such as the alkylammonium ions. Obviously this treatment adds to the cost of the clay but, on the other hand, the latter are relatively cheap as raw materials. It is important to note the surface treatment task is not only to render the clay an organo-clay, improving the wetting characteristic with the apolar polymer, but it is to increase the interlayer distance as well. Clearly, as the amount of carbon atoms in the tail of the ammonium ion increases, the clay becomes more organophilic; furthermore, the introduction of a longer organic molecule in the clay structure helps to increase the interlayer distance.
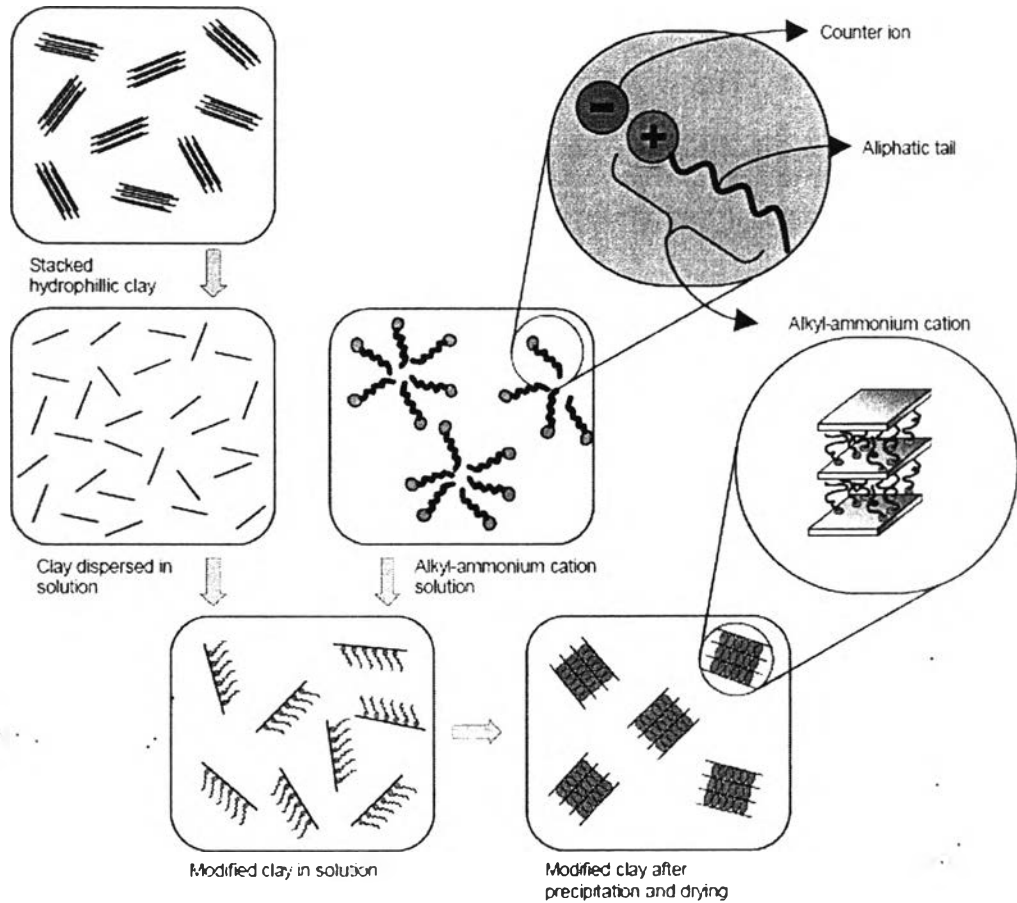
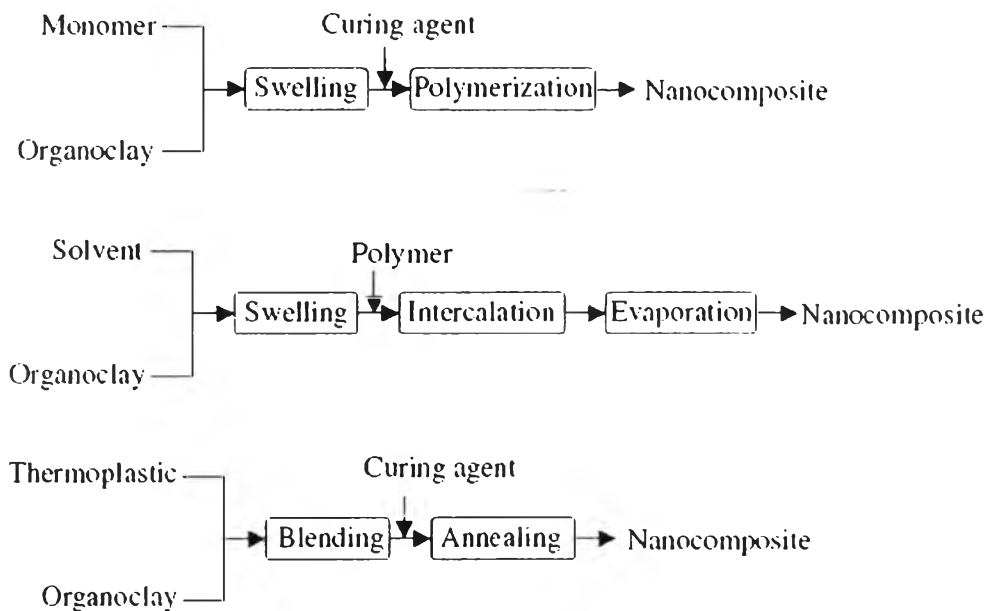**Figure 2.6**   Schematic representation of clay surface treatment.

From M.S.Thesis (2006), Jirakittidul Y. studied two types of nanoclays which were obtained from different location and had different CEC values, were modified with four types of alkylammonium ions via ion exchange reaction. The effect of the alkylammonium ions structures on organoclays was studied including the effect of primary alkylammonium ion as stearylamine (SA), tertiary alkylammonium ion as dimethyl stearylammonium bromide (DMS), quaternary mono alkylammonium ion as trimethyl octadecylammonium bromode (TMS), and quaternary dialkylammonium ion as dimethyl distearylammonium bromide (DMDS). The effect of cationic surfactant on two different types of nanoclays between sodium activated bentonite (BEN) from Thailand and sodium montmorillonite (MMT) from Japan were compared. The results showed that MMT had higher CEC value than CEC value of BEN, higher CEC value would result in higher chance for ion exchange re-

action to occur resulting in higher surfactant content in the interlayer spacing. The basal spacing of organo-BEN was less than that of organo-MMT, further less packing of alkylammonium ions in interlayer. Dialkyl tails structure (DMDS) was more effective to intercalate silicate layer than monoalkyl tail structure (TMS). Nanocomposites of organomodified nanoclays with DMDS, the structure of surfactant might interfere with the grafting reaction.

Phandee A. (2006) was also studied effect of surfactant structure on nanoclays and PP reactive nanocomposites. Na-bentonite (local clay mineral) and Na-montmorillonite were treated with several kinds of quaternary alkylammonium cations such as dihydrogenated tallow dimethylammonium chloride (DTDM), methyl di-(palm carboxyethyl)-2-hydroxyethyl-ammonium methylsulfate (DCEM), methyl di-[(partially hydrogenated) tallow carboxyethyl]-2-hydroxyethyl ammonium methyl-sulfate (DOEM) and methyl bis-(soya amidoethyl)-2-hydroxyethylammonium methylsulfate (DOAM) by ion exchange reaction for use as a nano-reinforcement. The effect of the molecular structure and functional groups of the surfactants on the organoclays was investigated by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and an FT-IR spectrometer. It was shown that the different molecular structure and the functional groups of the surfactant influence the interlayer spacing of the clay layer and the interlayer structure of the intercalated alkylammonium silicate.

2.6 Polymer-Clay Nanocomposites Preparation

There are several processes to make polymer/clay nanocomposites, including *in-situ* polymerization, solution exfoliation and melt intercalation. As shown in Figure 8, each technique consists of several steps to achieve polymer nanocomposites and begins with organoclays or sometimes pristine clays. In this thesis, the melt intercalation will be used, layered clays are directly mixed with the polymer matrix in the molten state (Zeng *et al.*, 2005). This technique, is environmentally benign due to no solvent is required and the absence of chemical reaction. Moreover, it is compatible with current industrial process, such as extrusion and injection molding.

Monomer ── ┐
                    Curing agent
                         │
                         ▼
        ──► Swelling ─►► Polymerization ─► Nanocomposite

Organoclay ── ┘

Solvent ── ┐
                    Polymer
                         │
                         ▼
        ──► Swelling ─►► Intercalation ─► Evaporation ─► Nanocomposite

Organoclay ── ┘

Thermoplastic ── ┐
                    Curing agent
                         │
                         ▼
        ──► Blending ─►► Annealing ─► Nanocomposite

Organoclay ── ┘

Figure 2.7 Flowchart of three processing techniques for clay-based polymer nano-composites: *in-situ* polymerization (upper), solution exfoliation (middle) and melt intercalation (bottom).

When layered clays are filled into a polymer matrix, either conventional composite or nanocomposite (Figure 9) can be formed depending on the nature of the components and processing conditions. Conventional composite is obtained if the polymer can not intercalate into the galleries of clay minerals. The properties of such composite are similar to that of polymer composites reinforced by microparticles. There are two extreme nanostructures resulting from the mixing of clay minerals and a polymer providing a favor conditions (Zeng *et al.*, 2005). One is intercalated nano-composite **(I)**, in which monolayer of extended polymer chains is inserted into the gallery of clay minerals resulting in a well ordered multilayer morphology stacking alternately polymer layers and clay platelets and a repeating distance of a few nano-meters. The other is exfoliated or delaminated nanocomposite **(II)**, in which the clay platelets are completely and uniformly dispersed in a continuous polymer matrix. However, it should be noted that in most cases the cluster (so-called partially exfoliated) nanocomposite **(III)** is common in polymer nanocomposites.
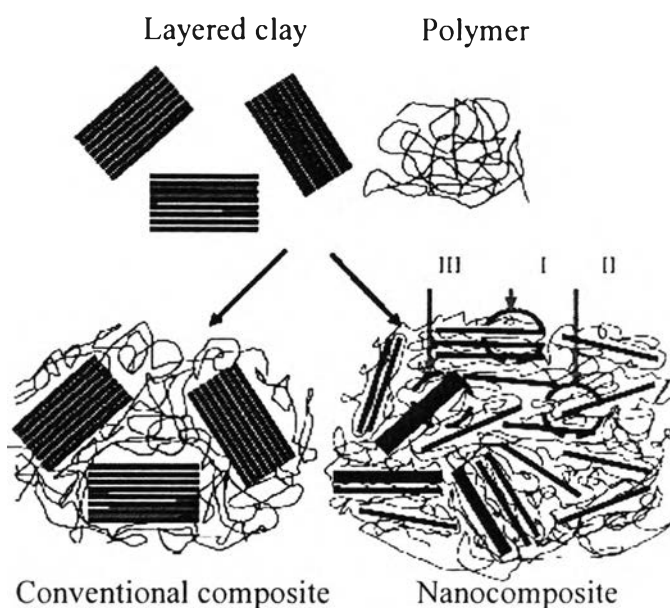
Figure 2.8 Schemes of clay-based polymer composites, including conventional composite and nanocomposite with intercalated (I), exfoliated (II) or cluster (III) structure.

2.7 Polymer Intercalation and Compounding by Using Compatibilizer

The process of modification of interfacial properties of an immiscible polymer blend leading to the creation of a new blend, which is called compatibilization, has played an important role in the development of polymer blends. Compatibilization by addition of a third component can significantly improve the mechanical properties of the blend by reducing the dispersed phase domain size and by enhancing phase adhesion (Ismail *et al.*, 2002).

However, in the case of PP, it is frequently necessary to use a compatibilizer. The use of a compatibilizer, namely a chemical able to render compatible two different materials, made it possible for the melt intercalation technique to be accepted as the most promising approach leading to polymer-clay nanocomposites formation. In this way the use of solvents and dedicated processes could be avoided providing a formation procedure which is both environmentally and user friendly. It is important, at this point, to clarify that the surface treatment and the compatibilizer are two different, independent and complementary ways adopted to solve the prob-

lem of poor miscibility between PP and clay. Through the surface treatment it is possible to change the interlayer structure of clay both increasing the gallery gap and modifying the silicate surface in an organic fashion, but this artifice is not enough to render compatible matrix and filler: the polarizing compatibilizer needs to be introduced in the PP.

In 2003, Garcá-López *et al,.* studied effect of compatibilizing agent on clay dispersing base on PP/clay nanocomposites. In this work, two different polar coupling agents, diethyl maleate grafted PP (PPgDEM) and commercial maleic anhydride grafted PP (PPgMA) were used. Diethyl maleate (DEM) as compatibilizing agent were used because of its high thermal stability, high boiling point and good compatibilization with polyolefins, compared with other compatibilizing agents. Furthermore, the low homopolymerization behavior of DEM, allowed a better control of the functionalization reaction. Maleic anhydride (MAH) was widely used as compatibilizing agent for this kind of systems and it was used as reference on this work. The PP-clay nanocomposites were prepared by melt compounding with two different clays, commercial modified montmorillonite, and sodium bentonite (BNa) modified with octadecylammonium ions. The relative influence of each factor, matrix and clay modification, could be observed from structural analysis (SAXS, TEM) and mechanical properties. Although the commercial clay outperformed octadecylammonium treated bentonite, differences in mechanical properties when using different clays were smaller if DEM was used instead of MAH. This was a consequence of the very low degree of compatibilization between the polymer matrix and the clay. Clay dispersion and interfacial adhesion were greatly affected by the kind of matrix modification. DEM had a lower polarity compared with MAH, provided a less effective interaction with the polar components of the clay. The reactivity of MAH towards the modifying agent was greater than in the case of DEM. Both factors, matrix and clay modification gave as result better interfacial adhesion and subsequent mechanical performance for MAH nanocomposites. Clay and matrix modification were synergistic factors which need to be properly modulated in order to obtain the desired final properties on this kind of non-polarpolymer based nanocomposites.

Further study by Ismail *et al,.* (2002), four types of compatibilizers (Surlyn[®], ethylene vinyl acetate (EVA), sodium salt hydrate of 4 styrenesulfonic acid

(4ssa, ssh)) with concentration of 7.5% w/w were chosen for this study in an attempt to improvements in properties through an affinity and polarity concept. Polystyrene-block–poly(ethylene–butylene)-block–polystyrene (SEBS), on the other hand, was chosen owing to the possible affinity with both components of a PS/PP blend: PS with PS blocks of SEBS and PP with polyolefinic block EB of SEBS. The effects of these compatibilizers on mechanical properties of PS/PP blends were investigated. Blends of 20/80, 50/50 and 80/20 (wt%) were prepared through melt blending in a single screw extruder at a blend temperature of 200°C and a screw speed of 40 rpm. It could be concluded that those blends with SEBS produce an improvement in toughness of PS/PP blends for all blend compositions, but values not exceed that of pure PP. The increase in toughness was accompanied by an increase in elongation at break. The addition of SEBS to the PP rich blend had a pronounced effect with the area under the stress–strain curve, i.e. the work to fracture was larger than that found for intermediate or PS-rich blends. This effect was observed for several blends consisting of a ductile matrix and brittle particle. Moreover, the brittle behavior could be converted into a quite ductile material in 50/50 and 80/20 PS/PP blend with the addition of SEBS. Surlyn® was chosen with the hope of achieving improvements in properties through both affinity and polarity concepts. The affinity was implied by the adhesion of PP with polyolefin of Surlyn®. The addition of Surlyn® increased the tensile strength of blend due to the improvement of adhesion and better stress transfer within the blend. Moreover, Surlyn® also improved Young's modulus of the blend because Surlyn® consisted of an ethylene backbone and pendant methacrylic acid groups, which were neutralized with metal. Although incorporation of low concentration of methacrylic acid into the ethylene backbone had little effect on properties, the neutralization of these groups had more dramatic influence, especially on improving the stiffness. In the case of adding of EVA in PS/PP blend, the results indicated that a slight improvement in elongation at break was obtained because the lack of tensile strength due to a reduction of the crystallinity of the blend as a result of the presence of vinyl acetate. whereas incorporation of 4ssa, ssh had reduced the properties in all blend compositions.

Incidentally, Tassanawat S. (2006) studied the processing of pH-sensitive material used for milk packaging based on polypropylene/organoclay nanocomposites

incorporated with indicator dyes. The nanoclay composites with indicator dyes were compounding through a twin screw extruder using Surlyn® as a compatibilizer. The nanoclay composites were fabricated into the sample sheet for the color testing and characterizations including thermal and mechanical properties. Milk deterioration was assessed for titratable acidity (TA), and color changes of the films were measured and expressed as Hunter values as well as total color difference (TCD). TCD values of BMB (Bromothymol blue) and BP (Bromocresol purple) type-films also changed continuously with the response of the film. The color changes of the films correlated well with TA value of fresh milk. According to the changes in Hunter color values of the films within the packages of fresh milk during storage at ambient temperature, the result showed that the color of BMB type-film turned from green to yellow whereas those of BP type-film turned from violet to green. The color changes of the developed indicator properly represented the degree of deterioration of fresh milk. Consequently, the nanocomposite indicator film could be employed as an effective smart packaging technology for evaluating fresh milk.

In this thesis work, a system made up of three components, polypropylene, organoclay and indicator dye was fabricated. Polypropylene was selected as the matrix due to its low cost, great processibility and wide range of applications. However, due to its disadvantages such as low toughness and low service temperature, the organoclay as the second component was needed to be introduced to overcome these problems. For modification of clay, Dipalmitoylethy Hydroxyethylmonium Methosulfate exhibited the largest interlayer spacing, promising the most suitable choice for producing PP/clay nanocomposites. The nanoclay composite film was produced by compression molding machine after melt compounded by using a twin screw extruder and Surlyn®, as a reactive compatibilizer. Furthermore, pH indicator film was laminated on the layer of nanocomposite film by using laminating machine. Subsequently, the pH sensor films based on polymer/clay nanocomposite was color tested.