CHAPTER I
INTRODUCTION

A smart packaging is recently a novel innovative. Its performance is useful for containing agricultural products and monitoring their spoilage. Since Thailand has been an agricultural country for a long time and majority of Thai people still works in agriculture and farming until the present, there are plentifully agricultural products a year, e.g. meat products, fruits, and vegetables flowers. In addition, these products need distributing to the domestic market including the foreign area.

One of the most important issues is an inevitable deterioration of the products before reaching consumer. This is because of time-consuming transportations and age-limiting products. A lot of researchers have been seeking a new packaging having competence in overcoming the issue. To fulfill the above goals, certain components are deliberately combined with the packaging such as antimicrobial agents, oxygen and ethylene scavengers as well as real-time monitoring sensors, etc.

The smart packaging is actually an alternative. It can lessen the problem because the packaging has a high level of proficiency in not only maintaining the freshness and prolonging the shelf-life of the product, but monitoring the deterioration of them as well. Such a smart packaging consists of two functions; active function and intelligent or sensor function (Murphy *et al.*, 2003).

The active packaging plays a crucial role in food preservation and permits the package to directly contact with food and the environment. Polypropylene (PP) is presently used as a packaging film. Owing to very good moisture barrier properties, PP can prevent the water and oxygen permeability into the film. Therefore, the barrier properties can be improved by adding a nanoclay namely sodium-bentonite in order that the clay will help holding the penetration of gas through the packaging. Such properties have a great effect on prolonging shelf-life of agricultural products because of a lowering respiratory rate of products causing a low accumulation of ethylene gas within packaging.

There are certain additives added into active films. They can kill some microorganisms taking place in the packaging. Silver nanoparticles, the effective antimicrobials, are incorporated into active films to enhance mechanical and barrier properties as well as to prevent the photodegradation of plastic (Puligundla *et al.*, 2012). Therefore, this previously mentioned factor also helps slowing down the senescence of the product.

The other function of a smart packaging is so-called an intelligent or a sensor film. The intelligent packaging is commonly used as a visual indicator because it offers possibilities enhanced to monitor the quality of product. Nowadays, people are currently concerning about the food safety. A natural dye from sappan heartwood is chosen as a suitable option for producing the sensor film because its chemicals is quite safer than that of synthetic dyes and its color easily shifts in response to change in pH within the food packaging. Accordingly, this natural dye does not have any adverse effects on human health as well as the change of colors can be detected by naked eyes. To conclude, their color is possibly able to be applied as a pH-sensoring film for agricultural products.

The well-defined purpose of the research is to prepare polymer nanocomposite films performing as an active film having good gas barrier and antimicrobial properties as well as an intelligent film having pH-sensitive property. Polymer-clay nanocomposites can be prepared by using different methods, including pre-polymer from solution or intercalation of polymer, in situ intercalative polymerization and melt intercalation (Ray and Okamoto, 2003). The preferred process is melt mixing by reason of environmentally benign manufacturing (Lin *et al.*, 2006).

In this research, for the dispersion of unmodified clay in the active film is not fine resulting in poor gas barrier film, sodium bentonite has to be primarily modified its surface via silanation process by using γ-methacryloxypropyltrimethoxysilane (γ-MPS) before grafting with polypropylene so that MPS will help enlarging the interlayer of clay and enhancing the interfacial adhesion between the modified clay and polypropylene. While PP-grafted modified clay is melting in the twin screw extruder, modified clay is likely to form intercalated and/or exfoliated structure in the nanocomposite due to a high shear atmosphere. To conclude, the obtained film provides a good barrier property because there is a good distribution of exfoliated nanocomposite bringing about the prevention from water and oxygen permeability.

In order to physically graft modified sodium bentonite onto PP, while the extrudate of modified bentonite and PP is exiting the die of the twin screw extruder, it is treated by a plasma generator under air atmosphere. On the contrary, so as to chemically graft the modified clay and PP, dicumyl peroxide (DCP), a chemical initiator, is chosen for chemical reaction during melt mixing in the extruder. Such both ways of preparation of polypropylene-clay nanocomposites are based on the inducement of free radicals at the end-functionalized MPS on modified clay and chain scission of PP resulting in the grafting of two components. The expected result of above means is to enhance the delamination of clay galleries, resulting in dispersion improvement of clay in polymer matrix. The hypothesis is verified by using a field emission-scanning electron microscope (FE-SEM) to observe the cryogenic-fractured surface of nanocomposites in terms of distribution and dispersion of clay in PP matrix and using an X-ray diffractometer (XRD) to reveal the nanostructure of PP-clay nanocomposites prepared by different modes. Moreover, the solvent extraction technique are applied for scrutinizing the promotion of favored interfacial adhesion, supported by silane functionalization equipped with a reactive processing—plasma based process and chemical reaction, between PP and modified clay.

Furthermore, the PP-clay nanocomposites are improved their antimicrobial functions by introducing silver nanoparticles into the interlayer space of the bentonite. Afterward, the silver nanoparticles-loaded bentonite (SBEN) was modified with organosilane prior to mixing. As silver nanoparticles have an extremely large specific surface area, this characteristic leads to increase their direct contact with microorganism cells, indicating the increasing effectiveness of antimicrobial property. Since the size of silver nanoparticles is very small (1-20 nm) and the size of microbial cell is far larger (100-1,000 nm) than that of nanoparticles, the nanoparticles are able to penetrate into the cell and then emit silver ions to merge with thiol, carboxyl, and hydroxyl group in the cell for deactivation of the following functions:

- Combine with a respiratory enzyme to cause a suffocation
- Bind with a protease enzyme and cause an indigestion
- Bind with DNAs and inhibit a cell replication

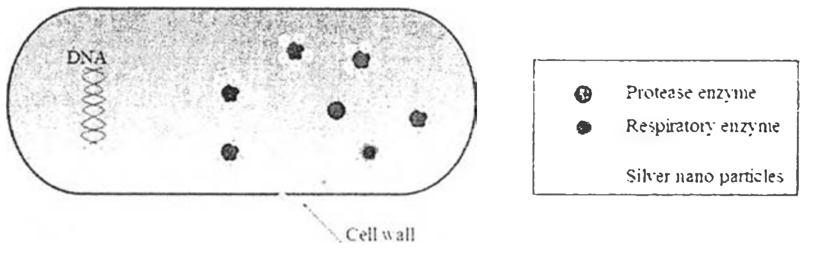

Figure 1.1 Mechanism of silver nanoparticles inhibiting microbial growth. (Nanos®, 2012)

After these functions are interrupted by silver nanoparticles, this consequent effect contributes to the damage of cell and finally the death of microbial cell. What's more, if the size of silver nanoparticles is sufficiently small, they tend to broaden their effectiveness. The size and shape of synthesized silver nanoparticles were determined by a transmission electron microscope (TEM). Lattice planes of silver nanoparticles and interlayer distance (d-spacing) of clay were analyzed by X-Ray Diffractometer (XRD).

The previously-mentioned PP-clay nanocomposites are considered as masterbatches of nanocomposites containing 5 wt% of clay. This research focuses on the effect of 1 wt% of clay in the nanocomposites. Thus, the as-prepared masterbatches were further mixed with PP in the extruder and finally blown to clear films for packaging application by blown film extrusion machine. The morphology of cryogenic-fractured surface of films is characterized by an FE-SEM. Besides, thermal properties of the films are also investigated by a differential scanning calorimetry (DSC) and a thermogravimetric analysis (TGA). Their application tests are investigated by gas barrier property determined by gas permeability testing—water vapor permeability rate (WVPR) according to ASTM E398 and oxygen transmission rate (OTR) accordance to ASTM D3985, mechanical properties tested by Lloyd universal testing machine (Lloyd-UTM) relating to ASTM D882. Finally, the antimicrobial properties are also studied against based on the agar disc diffusion against *Colletotrichum gloeosporioides* test based on ASTM G 21.

The other part of this thesis is to fabricate a film as a prototype for fish freshness indicator. Regarding to an intelligent film, consumers can monitor the quality of food and assess the safety of food by color detector. The films enable consumers to easily make up their mind to buy a fresh product because such sensor films render a great deal of essential information on quality and safety, and especially warning plausible problems to consumers. Especially, 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 so it is a reliable method for assessing the quality of fish during storage (Rukchon *et al.*, 2011).

At present, a number of people are apprehensive about the risk of synthetic dyes as freshness sensors in food packaging. A pollution of man-made pigments has become issues on carcinogenicity and environmental. Consequently, the use of natural dyes has gained a great of interests from worldwide researchers owing to its eco-safety (Lee *et al.*, 2008). With the characteristic chromophore and auxochrome, the natural dye extracted from Sappan wood (*Caesalpinia sappan* L.) is capable of easily turning to different shades of color to acidic and alkaline environments.

In the research, the sensor film was prepared by mixing the ethylene vinyl acetate (EVA), having 18 wt% vinyl acetate, and the sappan dye-carboxy methyl cellulose (SAP-CMC), from spray drying process, in the co-rotating twin screw extruder. The nanocomposite pellets were then hot-compressed to a thin sensor film. The obtained film is laminated onto the previously-prepared active films. Finally, the smart packaging was tested during the storage of fish based on the characterization of the change in color on the CIELAB system.