

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Theoretical Background

##### 2.1.1 Active Packaging

Active packaging contains active component allowing a controlled interaction between the food, package and internal gaseous environment, thus extends shelf life, improves fruit and vegetable safety or provides superior sensory quality.

Food condition in the definition of active packaging includes various aspects that may play a role in determining the shelf-life of package foods, such as physiological processes (e.g., respiration of fresh fruit and vegetable), chemical processes (e.g., lipid oxidation), physical processes (e.g., staling of bread, dehydration), microbiological aspects (e.g., spoilage by micro-organisms) and infestation (e.g., by insects). Through the application of appropriate active packaging systems these conditions can be regulated in numerous ways and, depending on the requirements of the packaged food, food deterioration can be significantly reduced.

Active packaging techniques for preservation and improving quality and safety of food can be divided into three categories; absorbers (i.e. scavenger) (Table 2.1), releasing system (Table 2.2) and other systems (Table 2.3). Absorbing (scavenging) systems remove undesired compounds such as oxygen, carbon dioxide, ethylene, excessive water, taints and other specific compounds (Table 2.1). Releasing systems actively add or emit compounds to the packaged food or into head-space of the package such as carbon dioxide, antioxidants and preservatives (Table 2.2). Other systems may have miscellaneous tasks, such as self-heating, self-cooling and preservation (Table 2.3).

Depending on the physical form of active packaging systems, absorber and releasers can be a sachet, label or film type. Sachets are placed freely in the head-space of the package. Labels are attached into the lid of the package. Direct contact with food should be avoided because it impairs the function of the system and, on the other hand, may cause migration problems.

**Table 2.1** Examples of sachet label and film type absorbing (scavenging) active packaging systems for preservation and shelf-life extension of foods or improving their quality and usability for consumers. Oxygen, carbon dioxide, ethylene and humidity absorbers have the most significant commercial use, lactose and cholesterol removers are not yet in use

Packaging Type	Examples of working principle/mechanism/reagent	Purpose	Examples of possible applications
Oxygen absorbers (sachets, labels, films, corks)	Ferro-compounds, ascorbic acid, metal salts, glucose oxidases, alcohol oxidase	Reduction/prevention of mould, yeast and aerobic bacteria growth Prevention of oxidation of fats, oils, vitamins, colours Prevention of damage by worms, insects and insect eggs	Cheese, meat products, ready-to-eat products, bakery products, coffee, tea, nuts, milk powder
Carbon dioxide absorbers (sachets)	Calcium hydroxide and sodium hydroxide or potassium hydroxide Calcium oxide and silica gel	Removing of carbon dioxide formed during storage in order to prevent bursting of a package	Roasted coffee Beef jerkey Dehydrated poultry products
Ethylene absorbers (sachets, films)	Aluminium oxide and potassium permanganate (sachets) Activated carbon + metal catalyst (sachet) Zeolite (films) Clay (films) Japanese oya stone (films)	Prevention of too fast ripening and softening	Fruits like apples, apricots, banana, mango, cucumber, tomatoes, avocados and vegetables like carrots, potatoes and Brussels sprouts

<b>Packaging Type</b>	<b>Examples of working principle/mechanism/reagent</b>	<b>Purpose</b>	<b>Examples of possible applications</b>
Humidity absorbers (dripabsorbent sheets, films, sachets)	Polyacrylates (sheets) Propylene glycol (film) Silica gel (sachet) Clays (sachet)	Control of excess moisture in packed food Reduction of water activity on the surface of food in order to prevent the growth of moulds, yeast and spoilage bacteria	Meat, fish, poultry, bakery products, cuts of fruits and vegetables
Absorbers of off flavours, amines, and aldehydes (films, sachets)	Cellulose acetate film containing naringinase enzyme Ferrous salt and citric or ascorbic acid (sachet)	Reduction of bitterness in grapefruit juice Improving the flavour of fish and oil-containing food	Fruit juices Fish Oil-containing foods Such as potato chips, biscuits and cereal products Beer
UV-light absorbers	Polyolefins like polyethylene and polypropylene doped the material with a UV-absorbent agent Crystallinity modification of nylon 6 UVstabiliser in polyester bottles	Restricting light-induced oxidation	Light-sensitive foods such as ham Drinks
Lactose remover	Immobilised lactase in the packaging material	Serving milk products to the people suffering lactose intolerance	Milk and other dairy products
Cholesterol remover	Immobilised cholesterol reductase in the packaging material	Improving the healthiness of milk products	Milk and other dairy products

**Table 2.2** Examples of sachet and film type releasing active packaging systems for preservation and shelf-life extension of foodstuffs or improving their quality. So far, none of these systems are in wide commercial use

<b>Packaging Type</b>	<b>Examples of working principle/mechanism/reagent</b>	<b>Purpose</b>	<b>Examples of possible applications</b>
Carbon dioxide emitters (sachets)	Ascorbic acid Sodium hydrogen carbonate and ascorbate	Growth inhibition of gram-negative bacteria and moulds	Vegetables and fruits, fish, meat, poultry
Ethanol emitters (sachets)	Ethanol/water onto silicon dioxide powder generating ethanol vapour	Growth inhibition of moulds and yeast	Bakery products (preferably heated before consumption) Dry fish
Antimicrobial preservative releasers (films)	Organic acids, e.g. sorbic acid Silver zeolite Spice and herb extracts Allyl isothiocyanate Enzymes, e.g. lysozyme	Growth inhibition of spoilage and pathogenic bacteria	Meat, poultry, fish, bread, cheese, fruit and vegetables
Sulphur dioxide emitters (sachets)	Sodium metabisulfite incorporated in microporous material	Inhibition of mould growth	Fruits
Antioxidant releasers (films)	BHA BHT Tocopherol Maillard reaction volatiles	Inhibition of oxidation of fat and oil	Dried foodstuffs Fat-containing Foodstuffs
Flavouring emitters (films)	Various flavours in polymers	Minimisation of flavour scalping Masking off-odours Improving the flavour of food	Miscellaneous
Pesticide emitters (the outer or inner layer of packaging material)	Imazalil Pyrethrins	Prevention of growth of spoilage bacteria Fungicidal or pest control	Dried, sacked foodstuffs, e.g., flour, rice, grains

**Table 2.3** Various other examples of active packaging systems

<b>Packaging Type</b>	<b>Examples of working principle/mechanism/reagent</b>	<b>Purpose</b>	<b>Examples of possible applications</b>
Insulating materials	Special non-woven plastic with many air pore spaces	Temperature control for restricting microbial growth	Various foods to be stored refrigerated
Self-heating aluminum or steel cans and containers	The mixture of lime and water	Cooking or preparing food via built-in heating mechanism	Sake, coffee, tea, ready-to-eat meals
Self-cooling aluminium or steel cans and containers	The mixture of ammonium chloride, ammonium nitrate and water	Cooling of food	Non-gas drinks
Microwave susceptors	Aluminium or stainless steel deposited on substrates such as polyester films or paper board	Drying, crisping and ultimately browning of microwave food	Popcorn, pizzas, ready-to-eat foods
Modifiers for microwave heating	A series of antenna structures that alter the way microwaves arrive at the food	Even heating, surface browning, crisping and selective heating	As above
Temperature-sensitive films	The gas permeability of the polymer is controlled by filler content, particle size of the filler and degree of stretching of the film	To avoid anaerobic respiration	Vegetables and fruits
UV-irradiated nylon film	The use of excimer laser 193 nm UV irradiation to convert amide groups on the surface of nylon to amines	Growth inhibition of spoilage bacteria	Meat, poultry, fish, bread, cheese, fruit and vegetables
FreshPad	Releasing natural volatile oils, absorbing oxygen and excess juice	Growth inhibition of bacteria Moisture control Self-life improvement	Meat
Surface-treated food packaging materials	Fluorine-based plasmas	Growth inhibition of bacteria	



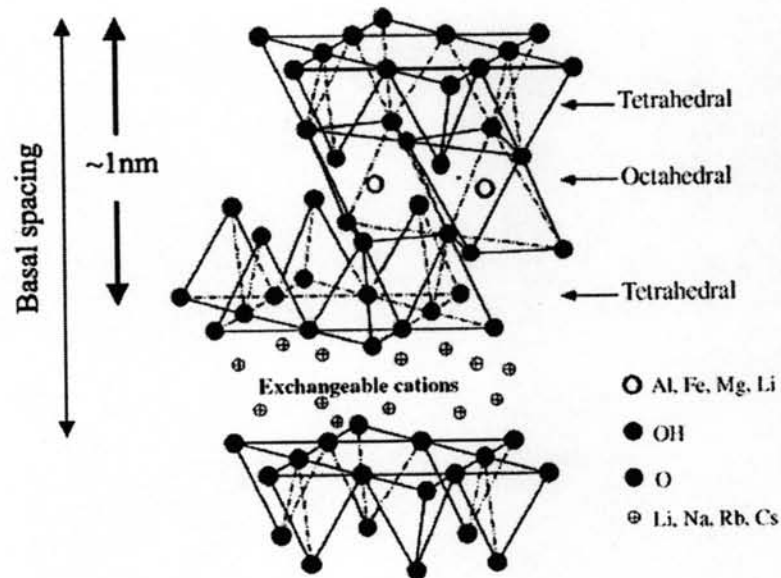
In this work the ethylene adsorbers is based on clay mineral and aluminium hydroxide disperse in the polymer film. Ethylene gas will be adsorbed on the clay mineral and form complex with aluminium hydroxide.

### 2.1.2 Structure of Silicate Clays

The silicate clays commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedron (the oxygen from the octahedral sheet also belong to the silica tetrahedral). The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 300 Å to several microns or larger depending on the particular clay. These layers stack with a regular van der Waals gap in between them called the interlayer or the gallery. Isomorphic substitution within the layers (for example,  $\text{Al}^{3+}$  replaced by  $\text{Mg}^{2+}$  or by  $\text{Fe}^{2+}$  in montmorillonite, or  $\text{Mg}^{2+}$  replaced by  $\text{Li}^+$  in hectorite) generates negative charges that are counterbalanced by alkali or alkaline earth cations (such as  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ) situated in the interlayer. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy.

Montmorillonite, hectorite and saponite are the most commonly used silicate clays. Their structure is given in Figure 2.1 and their chemical formula are shown in Table 2.4

This type of clay is characterized by a moderate negative surface charge (known as the cation exchange capacity, CEC and expressed in meq/100 g). The charge of the layer is not locally constant as it varies from layer to layer and must rather be considered as an average value over the whole crystal. Proportionally, even if a small part of the charge balancing cations is located on the external crystal surface, the majority of these exchangeable cations is located inside the galleries. When the hydrated cations are ion-exchanged with organic cations such as more bulky alkylammoniums, it usually results in a larger interlayer spacing.



**Figure 2.1** Structure of 2:1 phyllosilicates.

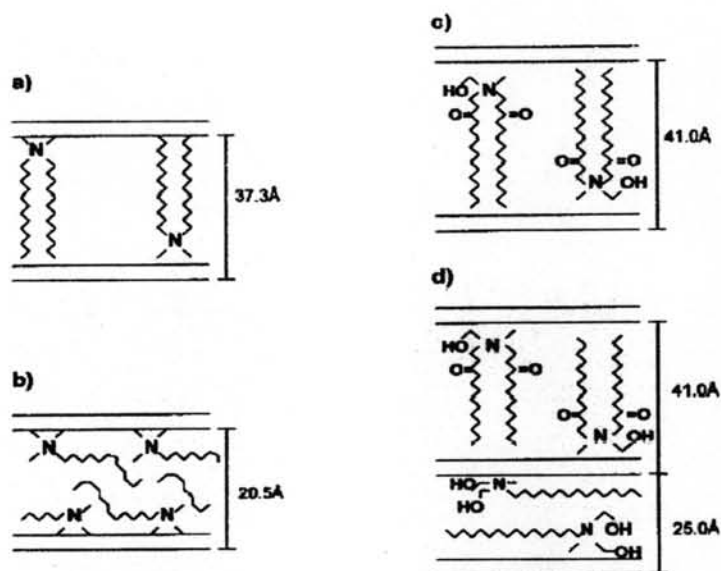
**Table 2.4** Chemical formula and characteristic parameter of commonly used 2:1 Phyllosilicates

2:1 phyllosilicates	Chemical formula	CEC (mequiv/100 g)	Particle length (nm)
Montmorillonite	$M_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$	110	100–150
Hectorite	$M_x(\text{Mg}_{6-x}\text{Li}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$	120	200–300
Saponite	$M_x\text{Mg}_6(\text{Si}_{8-x}\text{Al}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$	86.6	50–60

M: monovalent cation, x: degree of isomorphous substitution (between 0.5 and 1.3).

## 2.2 Literature Review

*Jin-Ho et al. (1997)* prepared organoclay complexes exhibiting hydrophilic as well as organo-philic natures by using several kinds of quaternary alkylammonium cations with different molecular structure and functional groups, teryldimethylammonium chloride (DMDS), methyltriethanoldipalmitylesterammonium methylsulfate (DCEM), monostearyltrimethylammonium chloride (ODTM), and methyltriethanolpalmitylesterammonium methylsulfate (DHMC), were incorporated into interlayer spaces. X-ray diffraction patterns for the dried organo-clay complexes. Upon intercalation, the basal spacing of DHMC-M expanded up to  $66 \text{ \AA}$ , indicating the incorporation of large surfactant molecules. On the basis of X-ray diffraction patterns and infrared spectra, the interlayer packing structures were proposed as shown in Figure 2.2. Among them, the formation of a regular interstratified structure for DHMC molecules (Figure 2.2d) might be due to the coexistence of DCEM molecules in the starting material as a competing guest species.



**Figure 2.2** The schematic diagrams of the possible interlayer structures of each quaternary alkylammonium derivative: (a) DMDS-M, (b) ODTM-M, (c) DCEM-M and (d) DHMC-M.



*Parija et al. (2004)* studied on physico-mechanical properties of the virgin PP and nanocomposites with different nanomer loadings. Thermal characteristics of polypropylene/layered silicate nanocomposites were also compared with those of the virgin polymer. Polypropylene/layered silicate nanocomposites were prepared from base polymer (10 MFI) and octadecylamine modified montmorillonite (1.30P nanomer), melt compounded with compatibilizer and without compatibilizer, i.e., maleic anhydride grafted polypropylene (Epolene-G3015). TEM analysis of the nanocomposites was carried out to study the dispersion of nanomer in the resulting hybrids. The experimental findings revealed a consistent improvement in the mechanical properties of the polypropylene/layered silicate nanocomposite for a relatively lower nanomer loading (3%) due to the reinforcing and toughening effect of nanoparticles. Addition of compatibilizer further enhanced the mechanical properties of nanocomposites because of the compatibilization of the clay and host polymer interface.

In 2005, *Ding C. et al.* prepare organophilic clay by using cetyl trimethyl ammonium bromide (CTAB) and PP/clay nanocomposites were prepared by using twin screw extruder. The PP graft in the formulation was 2 wt% relative to the amount of PP. The content of OMMT is relative to 100 phr polymeric matrix (PP and TMPP (PP solid-phase graft)). The flexural modulus of nanocomposites increases remarkably with OMMT content. The tensile strength, flexural strength and impact strength, however, reach a maximum at an OMMT content of 2 phr. The significantly increased mechanical properties at low OMMT loading may be due to the uniformly dispersed MMT tactoid with intercalated structures. TMPP promotes the dispersion of OMMT into PP matrix. The fraction of the intercalated structure decreases with the OMMT content. At higher content, aggregation of the OMMT may take place. As a consequence, the mechanical properties of the nanocomposite with higher OMMT content may decrease. The addition of OMMT does not affect the crystal structure of the PP matrix. The addition of TMPP has minimal effects on the crystallization behavior of PP. The crystallization peak temperature of PP/OMMT nanocomposite with 1 phr OMMT increases to 125.4 °C compared with 114.4 °C for neat PP. With more OMMT, the crystallization peak temperature stays above 120 °C. The DSC results clearly show that the addition of a small amount of OMMT into the PP matrix results in an increase of crystallization temperature. This phenomenon may be

due to the efficient nucleating effects of the silicate layers/tactoids. TMPP could improve the stability at high temperature while it shows adverse effect on the stability at lower temperature. All PP/OMMT nanocomposites show overall higher thermal stability compared with neat PP. The PP/OMMT nanocomposites show substantially improved initial thermal stability compared with neat PP. At relatively lower OMMT content, the initial thermal stability increases with OMMT content. The PP/OMMT nanocomposite with 4 phr OMMT shows the highest initial thermal stability. When the OMMT content is increased further (higher than 4 phr), the initial thermal stability decreases. This may be due to the aggregates of OMMT, which are less effective in blocking heat than the MMT layers/tactoids, increasing with OMMT content.

*Shah et al. (2005)*, Structure–property relationships for nanocomposites formed by melt processing from a series of organoclays and poly(ethylene-co-methacrylic acid) ionomers are studied. The chemical structure of the alkyl ammonium surfactants was systematically varied to determine how specific groups might affect the mechanical properties and morphology of these composites. Four distinct surfactant structural effects have been identified that lead to improved levels of exfoliation and higher stiffness for these nanocomposites: (1) higher number of alkyl tails on the amine rather than one, (2) longer alkyl tails instead of shorter ones, (3) 2-hydroxy-ethyl groups as opposed to methyl groups on the ammonium ion, and (4) excess amount of the amine surfactant on the clay instead of an equivalent amount. Most of these trends are opposite to what has been observed in nylon 6 based. It seems nylon 6 has a higher affinity for the silicate surface than does the poly(ethylene-co-methacrylic acid) ionomer while the latter is less repelled by the alkyl tails than the polyamide. Hence, surfactant structural aspects that lead to more shielding of the silicate surface or increased alkyl material leads to improved exfoliation in the ionomer. These observations are similar to those seen with LDPE and LLDPE based nanocomposites. It should also be noted that, although some organoclays were exfoliated better than others, none of the ionomer-based nanocomposites exhibited exfoliation levels as great as those seen in nylon 6 nanocomposites. Nevertheless, nanocomposites prepared from such ionomers offer promising improvements in performance and may be particularly suitable for barrier applications.

The effect of an organophilic bentonite on the thermal degradation of polypropylene was evaluated by *Ramos Filho et al. (2005)*. A polycationic bentonite clay (PB) was organically modified with a quaternary organic salt (cetyl trimethyl ammonium bromide) and added to isotactic polypropylene (PP). The compounds were prepared by melt intercalation using a twin extruder. The results showed that the modified clay had higher thermal stability in the solid state than the natural clay. This may be connected to a higher dispersion of clay particles, reducing oxygen diffusion through the sample.

In 1997, *Kawasumi et al.* studied the preparation of PP/ clay nanocomposites obtained by melt blending of PP, a maleic anhydride grafted PP oligomer (PP-g-MA), and clays modified with stearylammmonium using a twin-screw extruder. They found that there are two important factors to achieve the exfoliated and homogeneous dispersion of the layers in the hybrids: (1) the intercalation capability of the oligomers in the layers and (2) the miscibility of the oligomers with PP.

In 2005, *Gianelli W. et al.* shown the effect of the polymer matrix molecular weight on the possibility of producing by melt compounding nanocomposites based on PP homopolymers or heterophasic PP-PE copolymers and an organically modified montmorillonite, in presence of maleic anhydride-modified polypropylene (PP-g-MAH). An increase of mechanical properties was achieved both for homopolymers and heterophasic copolymers. However the reinforcing effect of clay dispersed in heterophasic copolymers was not as high as found for the homopolymers.

The thermogravimetric analysis of montmorillonite modified with the surfactant octadecyltrimethylammonium bromide was studied by *Xi. Y. et al (2004)*. There are four mass-loss steps. A mass-loss step is observed at room temperature and is attributed to dehydration of adsorption water. A second mass-loss step is observed over the temperature range 87.9 to 135.5 °C and is also attributed to dehydration of water hydrating metal cations such as Na<sup>+</sup>. The third mass loss occurs from 178.9 to 384.5 °C and is assigned to a loss of surfactant. The fourth mass-loss step is ascribed to the loss of OH units through dehydroxylation over the temperature range 556.0 to 636.4 °C.

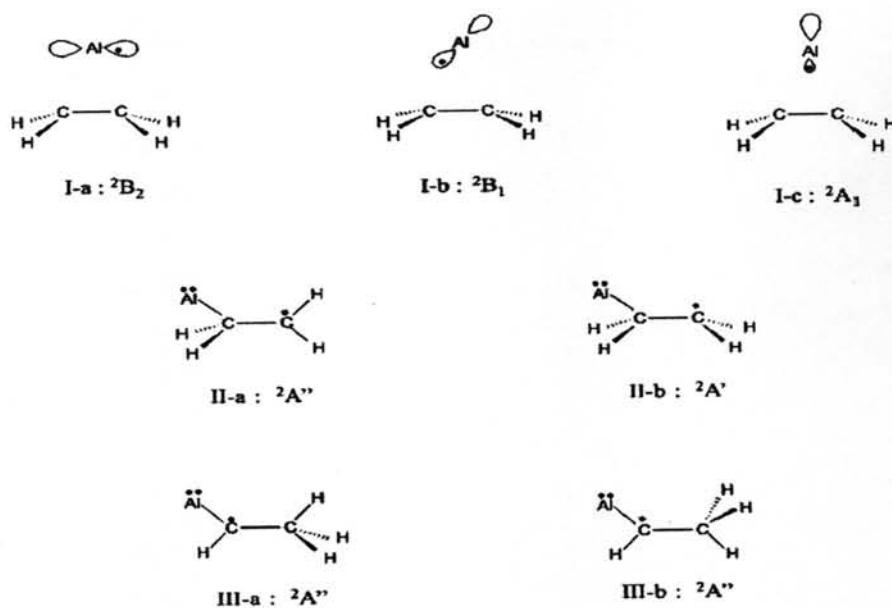
In 2006, *Othman N. et al.* studied the effect of compatibilisers on mechanical and thermal properties of bentonite filled polypropylene composites. Two types of compatibilisers namely; palm oil fatty acid additive (POFA) and polypropylene grafted-maleic anhydride (PPMAH) have been used in this study. The employment of compatibilisers, such as PPMAH and POFA is beneficial in aiding the mixing process of bentonite filled PP as indicated by the lower peak and stabilisation torque as compared to control composites. These positive effects of having compatibilisers in bentonite filled PP system would certainly increase the production rate coupled with low energy consumption during manufacturing process. The addition of PPMAH improves the interaction between bentonite and PP causing the stresses transferred from PP to bentonite to become more effective thus increasing the tensile strength of the composites. Apart from acting as processing aids both compatibilisers, POFA and PPMAH, used in this research have also enhanced the energy absorption capability of the composites as indicated by the increase in impact strength. Morphological assessments provided by the SEM micrographs reveal that the increments in the impact strength are largely contributed by an extensive plastic deformation at the interface resulted from better dispersion of bentonite in PP matrix. From DSC thermograms obtained in this study, fusion enthalpy for both crystallisation (DHc) and melting (DHm) processes of composites with compatibilisers have significantly reduced as compared to control. The melting and cooling temperatures also reduced as compatibilisers are added into bentonite filled PP. Therefore, it can be explained that the crystallinity of PP decreased with the presence of compatibilisers. The thermal stability of bentonite filled PP composites was improved with the addition of compatibilisers, POFA and PPMAH.

*Wang Y. et al.* (1998) determined oxygen and ethylene permeabilities for three kinds of polyethylene films (LDPE, LLDPE and HDPE) at 19°C and in the temperature range 4±30°C for LDPE. At constant temperature, ethylene and oxygen permeabilities decrease with increasing density. The temperature dependence of oxygen and ethylene permeabilities was found to be Arrhenius in the temperature range tested, with activation energies of 47.7 and 44.1 kJ/mol for ethylene and oxygen respectively. Permeabilities were found to be independent of film thickness and oxygen and ethylene permeabilities were independent of the composition of oxy-



gen/nitrogen mixtures. Gas permeabilities for zeolite-filled LDPE films were found to be larger than oxygen and ethylene permeabilities for unfilled LDPE film. The adsorption isotherm of ethylene on the ceramic component of the films has been measured at room temperature: the absorption isotherm corresponds to monolayer adsorption and the adsorption capacity of the ceramic was measured as 3.06 mmol/g.

In 2003, Cristian *A.C.* and Krylov *A.I.* reported there are several bonding schemes of the Al-C<sub>2</sub>H<sub>4</sub> complexes that shown in Figure 2.3. The type of bonding in these structures ranges from covalent (i.e., resulting from a bonding overlap of orbitals of the fragments) to van der Waals (i.e., dominated by dispersion). The most significant differences between covalent and van der Waals interactions concern binding energies and equilibrium geometries. While covalently bound molecules have typical binding energies of about 100 kcal/mol and bond lengths smaller than 1.5 Å, van der Waals clusters are only bound by a few kcal/mol, and the distance between fragments is usually larger than 2 Å. From a chemical point of view, the defining characteristic of van der Waals complexes is the retention of the properties of the individual entities in the complex. The Al-C<sub>2</sub>H<sub>4</sub> complex has a  $\pi$ -bonded structure (I-a in Fig. 2.3). It involves two donor-acceptor bonds: one result from an electron migration from the  $\pi$  orbital of ethylene into the vacant *sp* orbital of aluminum and the other results from a back donation from the singly occupied *p* orbital of Al to the  $\pi^*$  orbital of the olefin. Structures I-c, II-a, and II-b have been ruled out by the features of the electron spin resonance (ESR) spectrum. The infrared spectrum of the Al-C<sub>2</sub>H<sub>4</sub> complex in solid argon is consistent with a C<sub>2v</sub> structure which has two equivalent CH<sub>2</sub> groups. Structures I-a, I-b, and I-c all satisfy this condition. The I-b isomer is readily ruled out since its weak van der Waals interaction is inconsistent with the observed decrease of the CC bond force constant (by about 33% relative to free ethylene), which is equivalent to a bond length increase of 0.12±0.02 Å.



**Figure 2.3** Possible isomers of the Al-C<sub>2</sub>H<sub>4</sub> complex. Isomers I-a, I-b, and I-c are of C<sub>2v</sub> symmetry. In I-a, the orbital that hosts the unpaired electron results from a positive overlap between a *p* orbital of Al and π\* of ethylene. In I-c, the unpaired electron occupies an orbital derived from the *sp* hybrid of Al and the π orbital of C<sub>2</sub>H<sub>4</sub>. In I-b, the unpaired electron is on the nonbonding Al *p* orbital. The σ-bonded complexes II-a, II-b, III-a, and III-b belong to the C<sub>s</sub> point group. II-a and II-b are ethylradical-like structures, while III-a and III-b have an aluminummethylcarbene structure.

In 2005, *Ristolainen N. et al.* studied the dispersity of organoclay and aluminium tri hydroxide (ATH) particles in the polypropylene matrix with two different of compatibilizers. PP-g-MA is a commercial and PP-co-OH was synthesized in the laboratory. When composites were prepared with one filler (ATH or organoclay), the adhesion between the filler the matrix was improved with both compatibilizers. And exfoliated nanostructure was achieved. When both fillrs were present in the composites, the two compatibilizers reacted in different ways: PP-g-MA preferably with the organoclay, producing an exfoliated and intercalated structure, whereas PP-co-OH embedded the ATH particles more profoundly and the structure of the organoclay was less exfoliated. The dispersity of the components affected the mechanical and



fire-retardant properties. The composites containing both fillers and compatibilized with PP-g-MA were tougher but less stiff than the PP-co-OH-compatibilized composites. The fire-retardant properties remained at the same level or were improved by the partial substitution of organoclay for the ATH particles. The nanostructure formed when organoclay and the ATH particles were present together resulted in char formation, with the result that the heat release rate and the total mass loss were reduced.