THEORY AND LITERATURE REVIEW

2.1 Polymer Clay Nanocomposites [1,10,11]

Currently, polymer clay nanocomposites are the most popular use in many fields because addition of nanoclay leads to an improvement in material properties, such as modulus, strength, heat resistance, flame retardancy and lowered gas permeability. There are many techniques to prepare polymer clay nanocomposites, for example, in situ polymerization, solution intercalation, melt intercalation, and template synthesis. Because melt intercalation is a good technique that no solvent is required, therefore this technique is widely used in polymer blending. The layered silicate of clay can be mixed with polymer matrix in the molten state. The polymer can crawl into the interlayer space and form nanocomposites. Two idealized polymer-layered silicate nanocomposites morphologies, intercalated and exfoliated, are obtained as shown in Figure 2.1
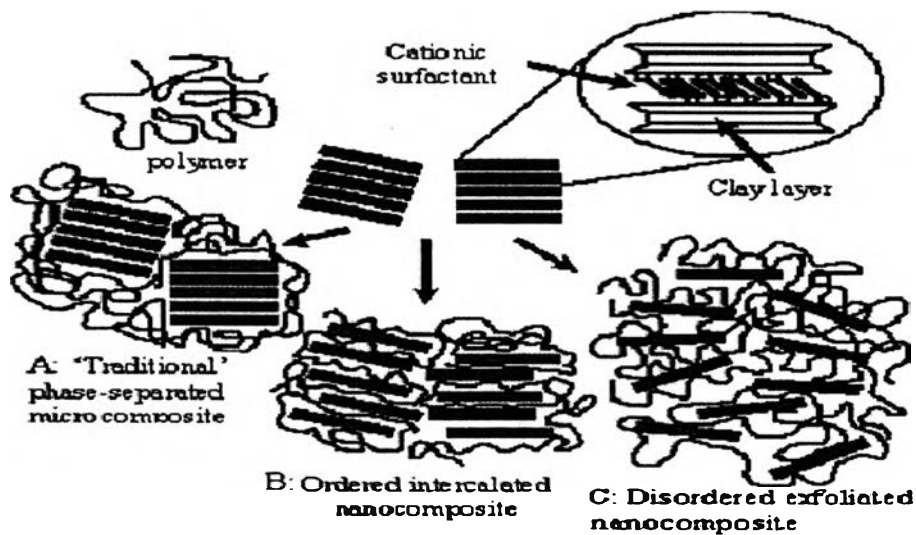

Figure 2.1 Intercalated structure and exfoliated structure [11]

Intercalated nanocomposites contain self-assembled, well-ordered multilayered structures where the extended polymer chains are inserted into the gallery space (2-3 nm) between parallel individual silicate layers. The delaminated or exfoliated nanocomposites result when the individual silicate layers are no longer close enough to

interact with gallery cations of the adjacent layers. In this case the interlayer spacing can be of the order of the radius of gyration of the polymer; therefore, the silicate layers may be considered well dispersed in the polymer. Both of these hybrid structures can coexist in the polymer matrix; this mixed nanomorphology is very common for composites based on silicates and clay minerals. The incorporation of polymer into layer of clay or polymer clay nanocomposites can increase the dimensional stability, thermal properties, and solvent resistance of the polymer matrix because of the nanometer-size particles of clay. In addition, they can be lower water sensitivity, reduce permeability to gases, improve flame retardancy and UV resistance, and so on.

Nanoclay is a term of clay mineral with a phylosilicate or sheet structure with thickness of 1 nm. Its property is hydrophilic. The clay surfaces can be modified with specific chemistries to be compatible with organic polymers. Surface areas of nanoclays are very large. When nanoclay is added to a host polymer, the resulting product is called a nanocomposite. Montmorillonite is a kind of clay that widely used in many applications. It consists of the layered silicates commonly used in nanocomposites. Its structure is known as the 2 : 1 phyllosilicates. Each layer consists of two sheets of silicate tetrahedral layer with an edge-shared octahedral sheet of either aluminosilicates or magnesium silicates (TOT structure). The layers are held together with a layer of charge cations such as Li^+, Na^+, K^+ and Ca^{2+}. These cations provide surface modification that required to disperse clays at the nanoscale into polymers as shown in Figure 2.2. They have relatively weak bonding between the layers.
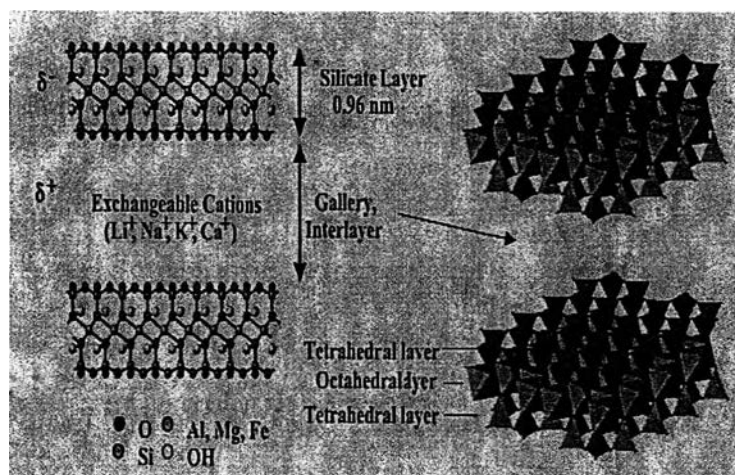

Figure 2.2 Structure of montmorillonite clay [10]

The clay is highly hydrophilic, therefore it is naturally incompatible with a wide range of polymer types. A necessary prerequisite for successful formation of polymer-layered silicate nanocomposites is therefore alternation of the clay polarity to make the modified clay or organoclay. It can be produced from normally hydrophilic clay by ion exchange with an organic cation such as a quaternary ammonium compound, alkylammonium ion, etc. For example, in montmorillonite clay, the sodium ions on the clay surface can be exchanged with an amino acid by cation exchange reaction as shown in equation 2.1 and Figure 2.3. During the reaction, as the montmorillonite clay is being converted to organomontmorillonite clay, it changes from hydrophilic in a nature to hydrophobic. After modification, its surface energy is lowered and is more compatible with organic polymers, therefore the organic polymers may be able to intercalate within the silicate interlayer of clay.
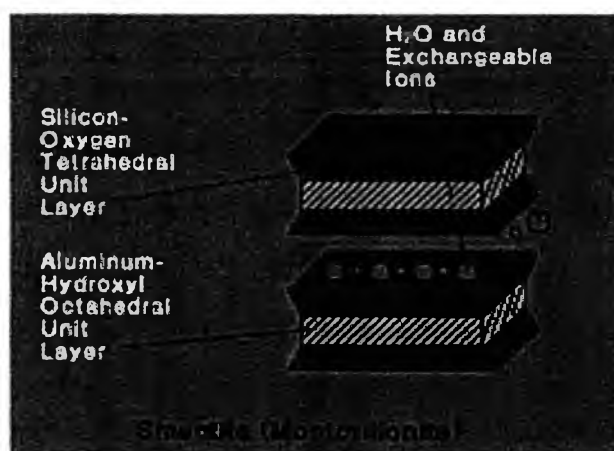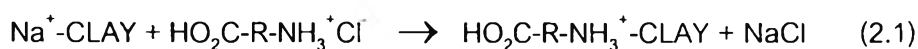
$$Na^+\text{-CLAY} + HO_2C\text{-R-}NH_3^+Cl^- \rightarrow HO_2C\text{-R-}NH_3^+\text{-CLAY} + NaCl \qquad (2.1)$$

Figure 2.3 Ion exchange reaction [11]

2.2 ABS [2,12]

ABS is an engineering plastic derived from acrylonitrile, butadiene, and styrene as displayed in Figure 2.4. The advantage of ABS is good mechanical strength, toughness, rigidity, and easy to processing. The important mechanical properties of ABS are resistance and toughness. Many modifications can be made to improve impact resistance, toughness, and heat resistance. It can be soluble in esters, ketones, and

ethylene dichloride. The aging characteristics of the polymers are largely influenced by the polybutadiene content, and it is normal to include antioxidants in the composition. ABS is considered superior for its hardness, gloss, toughness, and electrical insulation properties. However, it will be degraded when exposed to acetone. ABS is flammable when it is exposed to high temperatures, such as a wood fire. It will boil and burst spectacularly into hot flames; therefore flame retardant additives have been used to improve flame retardancy of ABS.
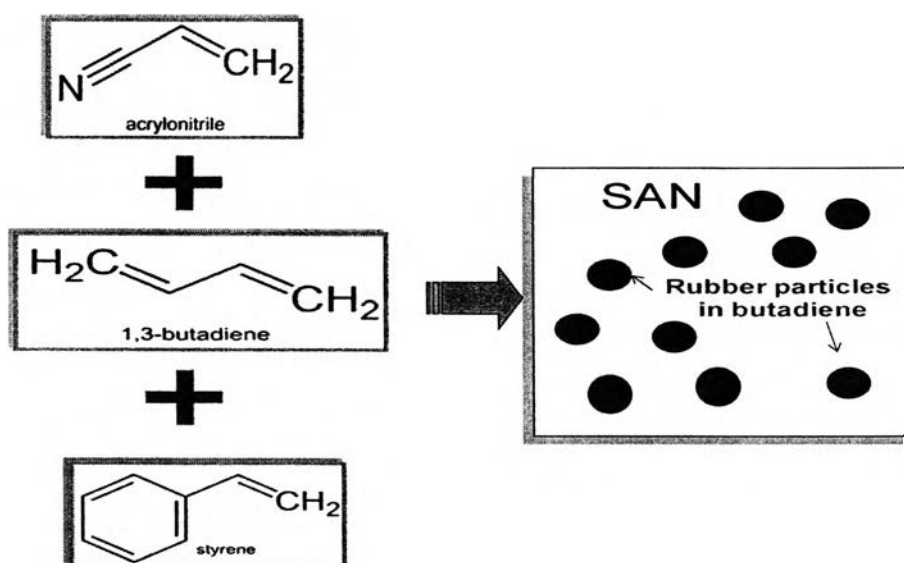
Figure 2.4 Acrylonitrile-butadiene-styrene copolymer

2.3 Flame Retardants [12-15]

The consumption of flame retardant additives in plastics around the world increases every year as shown in Figure 2.5. There are many applications to use flame retardant additives, for example, plastics are the biggest market to use flame retardant additives up to 66% for improving flame retardancy. Rubber industry is the second market next to plastics because carpet backing must be added with alumina trihydrate to improve its retardancy [12]. Flame retardants are used to identify grades of material which meet specific requirements when tested in accordance with flammability test procedures. The objective of flame retardant addition in plastics is to increase the resistance of a material to ignition and, once ignited, and to reduce the rate of flame spread (slow burning). The product does not become noncombustible, but use of a flame retardant additive may prevent a small fire from becoming a major catastrophe.
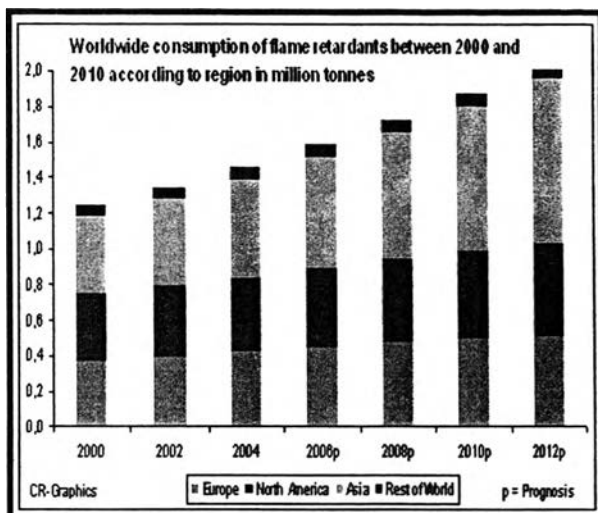
Product	Use (%)
Plastics	66
Textiles	5
Coatings/adhesives	3
Rubber	24
Wood/paper	2

Figure 2.5 Worldwide consumption of flame retardants between 2000 and 2012 [12]

2.3.1 Flammability of Polymers [6,13-15]

The flammability of polymers can be determined by their reactivity with oxygen. The limiting oxygen index (LOI), defined as the minimum amount of oxygen required to sustain combustion under specified conditions, is a quantitative measure of the tendency of materials to burn. In flame retardant system, study of the LOI can provide information on the effectiveness of flame retardant materials. Depending on the polymer and the applicable fire retardance standards, flame retardants are chosen to interfere with one or more stages of the combustion process: heating, decomposition, ignition, flame spread, smoke density. Fire retardants have to inhibit or even suppress the combustion process. In addition, UL-94 test was used to determine flame retardancy of polymer.

2.3.2 The Burning Process of Plastics [14]

The combustion of plastics is a process comprising many steps. A schematic representation of the various phenomena may be taken place during the combustion of plastics as shown in Figure 2.6.
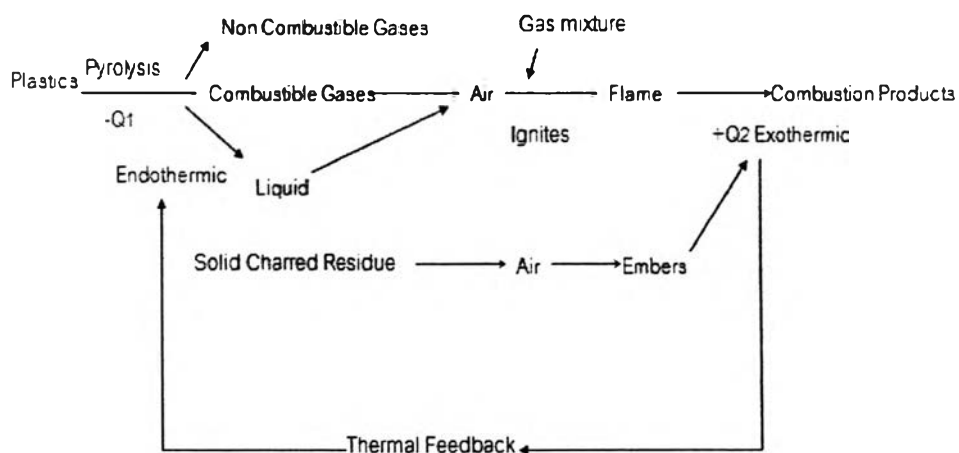
Figure 2.6 Combustion of plastics [14]

Three stages are necessary to initiate the combustion process as below.

2.3.2.1 Heating

The solid plastic is heated by an external source or by thermal feedback In this initial phase, thermoplastics tend to soften or melt and start to flow.

2.3.2.2 Decomposition

Decomposition is an endothermic process in which sufficient energy must be provided to overcome the high binding energies of the bonds between individual atoms. As the individual plastics differ in structure, their decomposition temperature ranges vary within certain limits. In most cases, decomposition occurs via free radical chain reactions, initiated by traces of oxygen or other oxidizing impurities, which are trapped in all plastics during manufacture. The oxidative degradation of polymers usually proceeds via the formation of hydroperoxide groups whose decomposition leads to highly reactive species such as H & OH radicals and thus to chain branching. These radicals are responsible for flame spread in the combustion process.

2.3.2.3 Ignition [13-15]

Flammable gases formed by pyrolysis, mix with atmospheric oxygen, and reach the lower ignition limit and are either ignited by an external flame or, if the temperature is sufficiently high, self-ignite. Ignition depends on numerous variables such as oxygen availability, temperature, physical and chemical properties of polymer. The reaction of the combustible gases with oxygen is exothermic and if sufficient energy is available, overrides the endothermic pyrolytic reaction and initiates flame spread.

2.3.3 Combustion of Polymers and the Combustion Cycle [14-15]

Combustion may be explained as the rapid uncontrolled reaction of oxygen with a substrate. The role of flame retardant additives is to:

- Slow down polymer combustion and degradation
- Reduce smoke emission
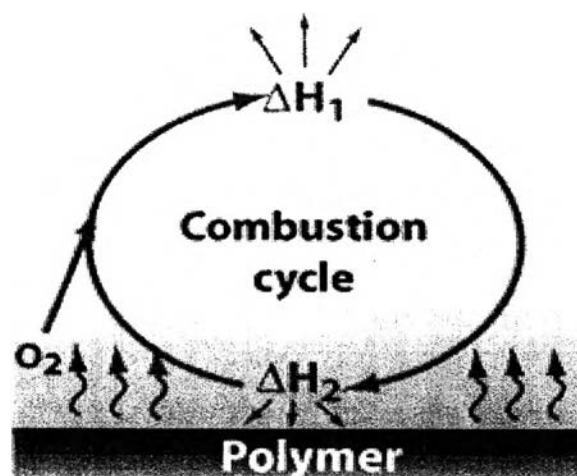- Avoid dripping of hot or burning material

Figure 2.7 Combustion cycle of polymer [15]

The combustion cycle as displayed in Figure 2.7 can be interrupted if the flame retardant additive is added in polymer matrix. Some mechanism of flame retardant additive displays the function as absorbers of heat, thus lowering the ambient temperature below the critical temperature for ignition. Others function by providing a vapor barrier that dilutes the concentration of the incoming oxygen required to feed the fire and thus slow down the kinetics of combustion. Another approach offering a barrier to combustion is to use materials that will crosslink or intumesce, providing a networked structure that prevents the ingress of oxygen to the site of combustion.

Dilution of the available fuel can be accomplished by the use of materials such as inorganic fillers that allow for the use of diminished amounts of the more combustible organic polymers. Another class of fire retardants consists of species that can interact with oxygen to form molecular species that in effect dilute the free radical character of oxygen and render it less reactive to the fuel source.

Physical characteristics of materials as well as chemical composition influence combustion behavior. Factors such as surface area, availability of oxygen to impinge on the site of ignition, heat transfer to and from the flame and also influence the rate and extent of combustion.

In general, the volatile components make a complex mixture, which ranges from simple molecules such as hydrogen and low molecular weight hydrocarbons to higher molecular weight species that can only volatilize at higher temperatures. Smoke particles are mainly of two kinds:

- Carbonaceous solid particles that produce black smoke, often called soot

- Liquid droplets that form as some gas molecules cool and condense producing light colored smoke.

The droplets explained above may also contain some divided solid materials such as minerals originally present in the combusting material; gases can also be entrained. The relative amounts of solids, liquids, and gases depend on the ambient conditions, particularly the temperature. There are two characteristics of smoke that deserve mention, namely toxicity and visibility.

2.3.4 Classification of Fire Retardant Additives [16]

The type of flame retardant and the quantity needed to meet specific objectives depend on the specific polymer. Additive as well as reactive flame retardants are available commercially. The addition of large quantities of a flame retardant may severely degrade the properties of the thermoplastic and also may present processing problems. Flame retardants that plasticize the polymer reduce thermal properties such as heat distortion temperature, whereas non-melting solid additives may severely degrade impact properties. Furthermore, many flame retardants have limited thermal stability and may place restrictions on processing temperature. Polymers containing high concentrations of filler may be difficult to process, and good dispersion may require special handling. The use of flame retardants in thermoplastics is therefore a compromise. The desired properties of a flame retardant additive are high decomposition temperature, low volatility, minimal effect on mechanical properties such as impact resistance, minimal effect on heat distortion temperature, good ultraviolet light resistance, absence of toxicity, and non-toxicity of combustion products.

2.3.4.1 Halogen-Containing Flame Retardants [13-15]

The mechanism of halogenated fire retardants depends on the reaction of halogen-based free radicals with excited-state fire propagating components in the gas phase. The choice of halogenated fire retardants depends on many factors such as polymer type and distribution of flame retardant additives in polymer matrix. The halogenated flame retardants can be combined with antimony trioxide in order to cause synergistic effect. The addition of antimony trioxide allows the formation of volatile antimony species (halides or oxyhalides), which interrupt the combustion process by inhibiting hydrogen radicals through the series of reactions. Because hydrogenhalide is released during combustion process, thus this halogenated flame retardant additive is limited to use because of toxic concerns.

2.3.4.2 Nitrogen/Phosphorus-Containing Flame Retardants [13-15]

The phosphorus is known to be an effective inhibitor of combustion process. It is found in both organic and inorganic materials that have flame retardant properties. Phosphate esters are widely used in PVC, modified polyphenylene oxide, polycarbonate/ABS blends, and cellulose acetate. The mechanism of phosphorus flame retardant additive as shown in Figure 2.8 depends on its chemical environment. The phosphorus species can form PO radical, P radical, and HPO radical that are capable of removing free radicals that can drive combustion. Ammonium polyphosphate is an efficient halogen-free flame retardant additive used in polyolefins (PE, PP), epoxy resin, polyurethanes, and unsaturated polyester phenolic resins. This compound is a non-toxic, environmentally friendly materials, and low smoke.
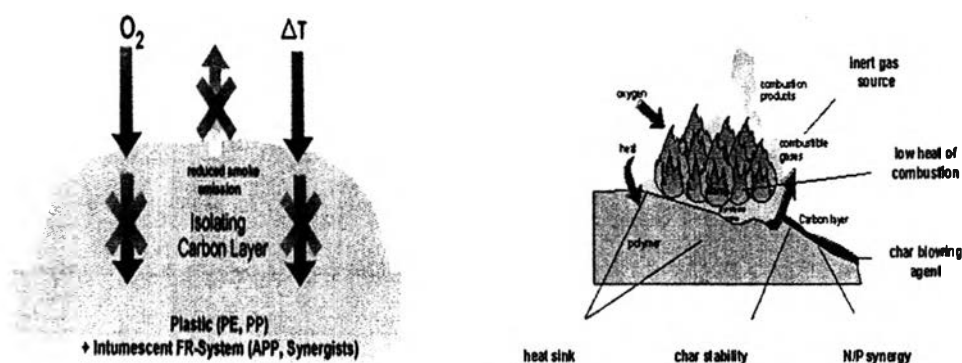

Figure 2.8 Mechanism of nitrogen/phosphorus-containing flame retardant [13]

2.3.4.3 Metal hydroxide-Containing Flame Retardants [13-15]

Metal hydroxides, especially aluminum trihydrate and magnesium hydroxide, are widely used in PVC, polyolefins, and ethylene propylene diene rubber. The mechanism of metal hydroxide-containing flame retardants as shown in Figure 2.9 is the release of water. This

leads to dilute the amount of oxygen and avoids the critical fuel/oxygen ratio. Furthermore, the ceramic-based protective layer is created during combustion, which improves insulation and gives rise to a smoke suppressant effect.
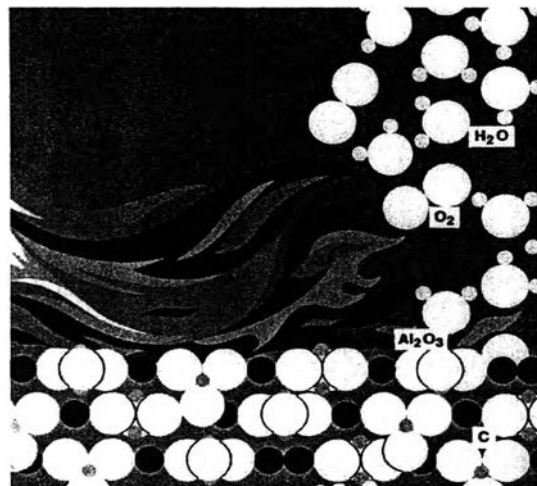

Figure 2.9 Mechanism of aluminum trioxide flame retardant [15]

2.3.4.4 Zinc/Boron-Containing Flame Retardants [13-15]

Zinc borate is a boron-based flame retardant with chemical composition of $(ZnO)_x(B_2O_3)_y(H_2O)_z$. The toxicity of zinc borate is low; therefore zinc borate is widely used as a flame retardant additive in PVC, polyolefins, elastomers, polyamides, and epoxy resins. Halogen-containing flame retardant additive is used in combination with other flame retardant additives such as antimony trioxide, aluminium trihydrate, phosphorus compounds.

2.3.4.5 Melamines [13-15]

Melamine (2,4,6-triamino-1,3,5-triazine), or melamine-derived flame retardants show excellent flame retardant properties, particularly of the intumescent type. The mechanism of melamine flame retardant additive is char formation. Melamine salts may act either as a source of

gases relatively stable to thermal oxidation occurring in the flame or as a source of stable char depending on the type of salt.

2.3.4.6 Silicon-Containing Flame Retardant [13-15]

Silicon-based materials are potential flame retardants as they produce protective surface coatings during combustion, resulting in a low rate of heat release. The mechanism of silicon-containing flame retardant additive is the formation of a silicon dioxide layer on the surface of the burning material, acting as a thermal insulator and preventing energy feedback to the substrate by reflecting the external heat flux radiation. During combustion, the silicon-containing flame retardant additive can form intumescent char that insulates the remaining substrate from heat and eliminates drip.

2.3.5 Mechanisms of Fire Retardant Action [13-15]

Flame retardants can act chemically and physically in the condensed phase and in the gas phase. The combustion is a complex process occurring through simultaneous multiple paths that involve competing chemical reactions. Heat produces flammable gases from pyrolysis of the polymer and if the required ratio between these gases and oxygen is attained ignition and combustion of the polymer will take place.

2.3.5.1 Physical Action [13-15]

- By formation of a protective layer

  The additives can form a shield that can decrease the heat transfer from the heat source to the material. Phosphorus additives may act in a similar manner as reported by Wilkie [16].

- By cooling

  The degradation reactions of the additive can play a role in the energy balance of combustion. The additive can degrade, which cools the substrate to a temperature below that required for sustaining the combustion process.

- By dilution

The incorporation of inert substances (e.g., fillers such as talc or chalk) and additives, which evolve inert gases on decomposition, dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded. Recent work by Ebdon et al [17] showed the insulating effect of a high amount of ash formed from silica-based fillers in flame retarded systems.

2.3.5.2 Chemical Action [13-15]

2.3.5.2.1 Reaction in The Condensed Phase This action consists of three processes as follow:

• Breakdown of the polymer, which can be accelerated by flame retardants, leads to its pronounced flow which decreases the impact of the flame.

• Flame retardants can leave a layer of carbon on the polymer's surface.

• Heat absorption through materials.

Flame retarding polymers by intumescence is essentially a special case of a condensed phase activity without apparent involvement of radical trap mechanisms in the gaseous phase. Intumescence involves an increase in volume of the burning substrate as a result of network or char formation. This char serves as a barrier to the ingress of oxygen to the fuel and also as a medium through.

2.3.5.2.2 Reaction in The Gas Phase

The radical mechanism of the combustion process, which takes place in the gas phase, is interrupted by flame retardant additives or its degradation. The exothermic processes that occur in the flame are stopped, the system cools down, and the supply of flammable gases is reduced and completely suppressed. For example, metallic oxides can act as flame inhibitors. The active radicals hydroxyl radical are adsorbed on the surface of oxide particles. A collision energy is transferred to the oxides and peroxy radicals, which are less reactive than the initial hydroxyl radicals formed.

2.3.6 Testing of Flame Retardant Plastics

Flame retardant additives are frequently designed to meet specific flammability tests. The laboratory tests used most frequently for thermoplastics are described below.

2.3.6.1 Limiting Oxygen Index [13-15]

This method was used to measure the ignition of material or pyrolysis products under given conditions of temperature and oxygen concentration. This testing provides a measure of flammability properties according to ASTM D 2863-77 which describes the test protocol for measuring oxygen index. The oxygen index test consists of a vertical glass tube 60 cm high and 8.4 cm in diameter, in which a clamp at its bottom end holds a rod or strip specimen vertically. A mixture of oxygen and nitrogen gas is metered into the bottom of the tube, passing through a bed of glass beads at the bottom to smoothen the flow of gas, providing a specific environment for the sample. The test places a sample 125 mm of length and 13 mm of width in a vertical position and it is ignited at its upper end with a flame, which is then withdrawn. The sample then burns like a candle from the top down as shown in Figure 2.10. The limiting oxygen index (LOI), is the minimum percent of oxygen in an oxygen-nitrogen mixture that will just sustain burning for 2 inches or 180 seconds, whichever comes first.
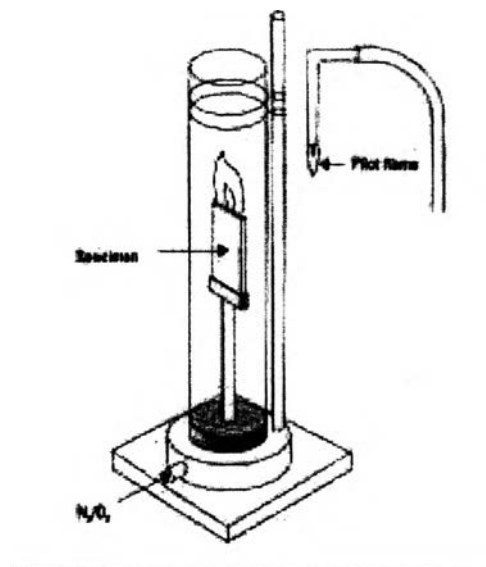
Figure 2.10 Limiting oxygen index testing [1]

2.3.6.2 UL 94 HB Horizontal Burning Test Procedure [13-15]

The flammability testing for plastic materials are UL-94 flammability performance designed by Underwriter's Laboratories Inc., USA. The material is ignited and self- extinguished. Several ratings can be applied based on the rate of burning, time to extinguish, ability to resist dripping and whether or not drips are burning. In general, materials that meet UL-94 HB grade are not recommended for electrical properties except for mechanical and/or decorative purposes. Sometimes misunderstood: materials that are not meant to be FR materials) do not automatically meet HB requirements. UL 94 HB is, although the least severe of flammability classification has to be checked by testing. The test places a sample 125 mm of length and 13 mm of width in a horizontal position over a standard Bunsen burner as displayed in Figure 2.11. The test measures burn rate in mm/min or inches/min. A sample should not have a burn rate exceeding 40 mm/min for thickness of 3 mm.
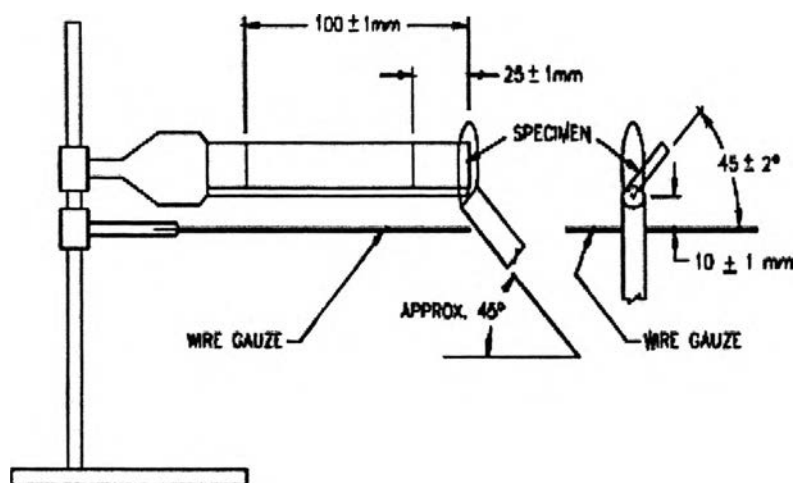
Figure 2.11 UL 94-HB horizontal testing procedure [1]

The vertical tests, as illustrated in Figure 2.12, take the same specimens as are used for the HB test. Burning times, glowing times, when dripping occurs and whether or not the cotton beneath ignites are all noted. Framing drips, widely recognized as a main source for the spread of fire or flames, distinguish V-1 from V-2. For UL-94V grade, the flame spread of samples were determined vertically as displayed in Figure 2.8 and the rating of V-grade was divided into 3 grades as shown in Table 2.1 and 2.2.
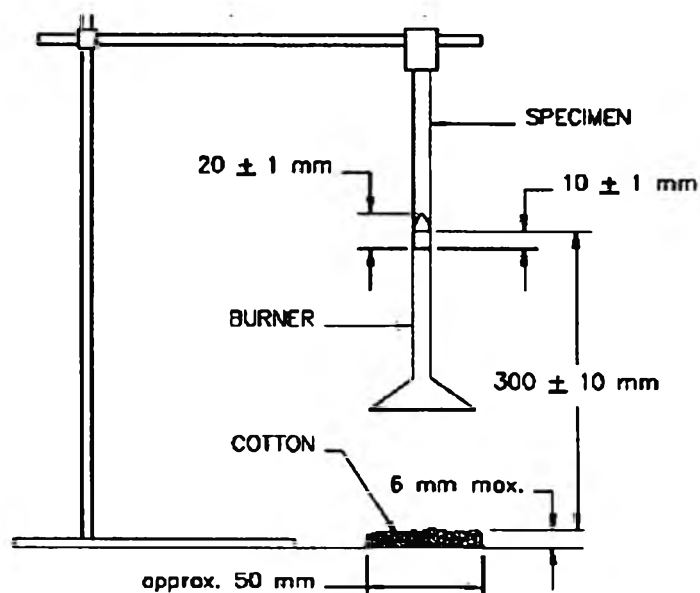

Figure 2.12 UL 94 V-0, V-1, and V-2 vertical testing procedure [1]

Table 2.1 Materials classifications for UL-94V

Criteria conditions	V-0	V-1	V-2
After flame time after first flame application (t_1) or after flame time after second flame application (t_2)	$\leq$10s	$\leq$30s	$\leq$30s
$t_1 + t_2$	$\leq$50s	$\leq$250s	$\leq$250s
t_2 + afterglow time after second flame application (t_3)	$\leq$30s	$\leq$60s	$\leq$60s
After flame of any specimen up to the holding clamp	No	No	No
Cotton ignited by flaming particles or drops	No	No	Yes

Table 2.2 The burning rate of UL-94 test

Rating	Test Criteria
UL-94.V-0	• The test samples are extinguished within 5 seconds average time • None of the test samples burn longer than 10 seconds • No test samples emit burning particles
UL-94.V-1	• The test samples are extinguished within 25 seconds average time (mean of 10 successive tests). • None of the test samples burned longer than 30 seconds • No test samples emit burning particles
UL-94.V-2	• The test samples are extinguished within 25 seconds average time (mean of 10 successive tests). • None of the test samples burrned longer than 30 seconds • The test samples emit burning particles during the test
UL-94.HB	• Horizontal test uses samples of a defined thickness which must not burn faster than 40 mm/min.

2.4 Silica and Silatrane

2.4.1 Silica [3-5]

Silica is found in the tissue of many plants. Almost all biogenic silica is amorphous. Plants can take up silica in dissolved form only. The silica is found in rice structure, i.e., husk, leaf-blades, leaf-sheath, and stems. The structure of silica in several plants has been displayed to consist of a dense gel with 1-10 nm of pore diameter. Table 2.3 shows the typical silica contents in some commercially used monocotyledons. The composition of silica in plants depends on agricultural methods, on geographical and weather.

Table 2.3 Silica contents in various plants [18]

Plant	Part	Ash content in g/Kg	Silica in ash in wt%	Silica content in g/Kg
Rice	Husk	200	96	192
	Straw	150	82	123
Wheat	Leaf sheet	110	91	100
Corn	Leaf blade	120	64	77
Barley	Straw	6	54	3
Oats	Straw	70	47	33
Bamboo	Nodes	20	57	11

2.4.1.1 Rice [3-5, 18, 19]

Rice is the staple food for about 2/3 of the world population. More than 500 million tons of world-wide rice is produced annually, of which 92% is harvested in Asia. In 1997, Thailand is a leader rice producing country which exports rice more than 6 million tons to various countries around the word. This report revealed that Thailand has potentially competition in both of rice

production and marketing when it was compared to other countries as shown in Table 2.4 and 2.5.

Currently, Thailand still exports large amounts of rice to other countries around the world; hence, rice millings that generate the largest quantity of by-products known as rice husk were found in lot of quantity. As rice husk or waste from rice millings was used as fuel, animal food, fertilizer, and brick making. This rice husk contains about 75% organic volatile matter and the balance of 25% of its weight is converted to ash during firing process known as rice husk ash (RHA). This ash is mainly silica that is a hard glassy mineral. About 7 million tons of rice husk are produced annually, therefore this rice husk causes damage to the land and surrounding area as dump. Presently, the waste rice husk was used as silica source, activated carbon production, and organic chemical production but only few applications in utilization of fertilizer. Nevertheless, the utilization of rice husk which is the appropriate way to dispose and solve pollution problem is researched and developed extremely.

Table 2.4 Cultivation area, total and average rice production in each period [18]

Period	Cultivation Area $(1600m^2)$	Total Production (1,000 tons)	Average Production $(Kg/1600m^2)$
1991/1992	59,671,000	20,400	361
1992/1993	60,453,000	19,917	348
1993/1994	59,251,000	18,447	348
1994/1995	60,677,000	21,111	376
1995/1996	63,353,000	22,016	387

Table 2.5 Area, total and average rice production in each country [18]

Country	Harvest Area (1600m^2)	Total Production (1,000 tons)	Average Production (Kg/1600m^2)
India	262,712,000	118,400	451
China	189,831,000	178,251	939
Indonesia	66,538,000	46,245	695
Bangladesh	61,562,000	46,245	447
Thailand	56,095,000	21,111	376

2.4.1.2 Corn [3-5, 18]

Corn is the third staple food next to wheat and rice. Currently, total corn production around the world is approximately 575.62 million tons. USA is the biggest production leader in the world. China is the second rice production and Europe is the third rice production in a rank. Thailand. Presently, total corn production in Thailand is about 507 Kg/1600m^2 or 4.40 million tons as shown in Table 2.6 and 2.7, respectively.

Table 2.6 Total corn production in each country [18]

Country	Production (million tons)		
	1994/1995	1995/1996	1996/1997
USA	256.26	187.31	236.06
China	99.28	112.00	117.00
European	28.30	29.06	37.78
Brazil	37.44	32.48	34.00
Mexico	17.01	17.78	19.00
Argentina	11.36	11.10	14.50
Thailand	3.97	4.16	4.40
Others	107.44	121.80	115.88
Total	561.42	515.69	575.62

Table 2.7 Cultivation area, total and average corn production in Thailand [18]

| Period	Cultivation area (1600m^2)	Total corn production (1,000 tons)	Average corn production (Kg/1600m^2)
1994/1995	8.83	3.97	449
1995/1996	8.35	4.16	498
1996/1997	8.67	4.40	507

2.4.2 Silatrane Complex [7-9, 20-23]

Silatrane is a pentacoordinate silicon derivative formed from the reaction of trialkanolamines such as triethanolamine with trifunctional silanes such as (RSi(OMe)$_3$) to yield highly crystalline, monomeric pentacoordinate silanes [7]. Si is a valent element connecting with inorganic or organic substituents. Silatrane structure is generally classified by the tricyclic model wherein a transannular Si-N dative bond is assumed to be present. The siloxane bond in silatrane structure is susceptible to alcoholysis under suitable condition. This compound is a great deal of interest because of its cage structure, physical/chemical properties, and especially biological activity and patterns of chemical reactivity [8-9, 20-23].

2.5 Silane Coupling Agent [13]

In order to improve silica dispersion into polymer matrix, silane coupling agents are widely used to modify the surfaces of silica. The silane couplings in commercial use are alkoxy-based and organic group attached to the silicon center, generally formula being Y-(CH$_2$)$_3$Si(OR)$_3$. The organofunctional group Y is bound to the silicon atom via a short carbon chain and links with the polymer. Bonding to the polymer takes place by chemical reactions or physicochemical interactions such as hydrogen bonding. The alkoxy groups can be hydrolyzed at the first stage, liberating the corresponding alcohol. Continuous reaction with water or moisture results in elimination of all OR groups as alcohol and their replacement by hydroxyl moieties to give silanol on their structure.

Organosilanes depend on the reaction with surface hydroxyl groups to produce a stable covalent bond and a stable layer on the filler surface, therefore they are effective on fillers with high amount of hydroxyls, especially silica, silicates, oxides, and hydroxides. For example, aminosilanes are widely use for surface treatment of fillers such as clay. Commercial silanes are based on γ-aminopropyl functionality. Their aqueous solutions are stable as a result of hydrogen bonding between the silanol groups and the primary amine. The amino group may absorb on surfaces and also show to be very prone to hydrogencarbonate salt formation with atmospheric carbon dioxide. Vinylsilanes have vinyl group attached to silicon atom. It is widely used with PVC, EPDM, EVA, etc.

Several years ago, in 1991, Laine *et al.* [7] have found new approach to synthesize organosilicon compounds directly from a very inexpensive starting material, silica, and ethylene glycol (EG) in only one step which synthesize tris(silatranyloxyethyl)amine from silica and triethanolamine as shown in eq. (2.2). When this reaction is performed on organosilsesquioxane substrate with triethanolamine as an alcoholic reactant, the yield of silatrane is high by this method.

(2.2)
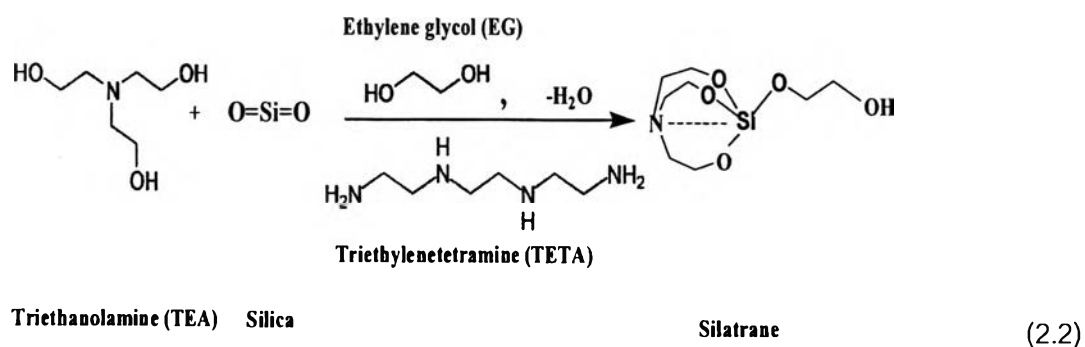
Therefore, the synthesized product is tractable neutral alkoxy compound providing novel route to use as silicon containing flame retardant additive in polymer blending.

2.6 Literature Review

Many researchers have been studied on synthesis of silatrane complex from low cost starting material. For example, In 1995 Punchaipetch [8] synthesized silatrane complex by one step reaction of silicon dioxide and triethanolamine with ethylene glycol as a solvent. The obtained compounds were formed through both condensation and ring opening polymerization to form the mixture of silatrane. Moreover, the synthesized purified product had high thermal stability. However, flame properties of silatrane complex has not been investigated.

Several years later, in 2003, Pipattanatornkul [9] synthesized silatrane and alumatrane via the Oxide One Pot Synthesis (OOPS). The silatrane complex, alumatrane complex, and octadecylammonium montmorillonite were used as flame retardant additives to PVC and Nylon12. These nanocomposites were prepared from melt blending process. The results of WAXD, TEM, and SEM showed the dispersion of inorganic additives in polymer matrices. However, the aggregation of silicate layers or silatrane agglomerates at high content loading indicated partially intercalated structure. The gross heat calorific value was reduced while limiting oxygen index value (LOI) was increased which led to enhance flame retardation. Moreover, the increasing of flame retardant additives content also improved mechanical properties.

Within the same year, Chuayjuljit et al. [19] prepared silica from rice husk ash by chemical treatment. The properties of rice husk silica were compared with commercial silica, Sylo-1. The rice husk silica had a smaller particle size and a higher specific surface area but a higher bulk density than those of Sylo-1 silica. Moreover, it was also found that LDPE film with rice husk silica showed similar properties to LDPE film filled with commercial silica in terms of its blocking behavior, mechanical strength, and film clarity.

From agricultural wastes and pollution problems, the use of green technology is also of great importance. Therefore, many researches have been attempted to use local

raw material as a filler in polymer in order to improve physical and mechanical properties because of its low cost. However, there have been no reports on the use of fillers produced from natural sources as a flame retardant in ABS plastics. In 1999, Owen et al. [24] studied mechanical, microscopical, and fire retardant properties of ABS composites. Antimony trioxide (Sb_2O_3) with brominated materials (i.e., octabromodiphenyl oxide, 1,2-bistribromophenoxy ethane, tetrabromobisphenol A, and poly-dibromostyrene) were used as an additive in ABS flame retardant formulations. It was found that the brominated materials had more influence than Sb_2O_3 on the fire retardant properties of ABS. The ABS nanocomposites increased the flexural modulus and reduced the deflection at peak force values, whereas the tensile modulus and strength were relatively unaltered with Sb_2O_3 loading. The impact strength of the ABS was affected by both additives as loading level and average particle size increased. The presence of 5 wt% sub-micron Sb_2O_3 caused a 20% reduction in impact strength whilst the reduction due to the brominated materials depended upon the specific halogenated compound used. Scanning electron microscopy showed good dispersion of Sb_2O_3 regardless of particle size and transmission electron microscopy revealed that Sb_2O_3 resided in the SAN phase of the polymer. Besides, the synergistic effect on flame retardancy was found when Sb_2O_3 was added with brominated materials.

Three years later, in 2002, Wang et al. [25] prepared ABS/montmorillonite nanocomposite using a direct melt intercalation technique. Its structure and thermal properties were characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HTEM), and thermogravimetric analysis (TGA). The results of HTEM showed that ABS/clay nanocomposite was a kind of intercalated-delaminated structure. The nanocomposite enhanced the formation of char and improved the thermal stability of ABS matrix as measured by TGA. This result derived from the pyrolysis of ABS which was divided into two steps. 5 wt% Organically montmorillonite (OMT) was kept a multilayered structure in the ABS matrix at 600°C in the first step. This carbonaceous char builded up on the surface during burning acted as insulator and slowed the escape of the volatile products generated during decomposition. In the second step (500-650°C), the loss of nanoABS was less than that of pure ABS. Thus,

the formation of the intercalated structure would also influence the second degradation step of nanoABS in the char layer.

Later on, In 2003, Wang *et al.* [26] synthesized polycarbonate (PC)/acrylonitrile-butadiene-styrene (ABS) polymer alloy/montmorillonite nanocomposites by direct melt intercalation technique in order to develop new alloys that have good thermal properties better than pure PC/ABS alloys. Their structure and thermal properties were characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HREM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). The results of XRD and HREM showed that nanocomposite was a kind of intercalated structure and the gallery heights of PC/ABS/MMT nanocomposites were almost the same as that of PC/MMT nanocomposite which had 3 nm interlayer spacing; meanwhile, the nanocomposites improved thermal stability of PC/ABS polymer alloy matrix.

In 2004, Wang *et al.* [27] prepared flame retardant ABS/organomontmorillonite (OMT) nanocomposites by direct melt intercalation technique. OMT was modified with hexadecyl trimethyl ammonium bromide by ion exchange reaction. Decabromodiphenyl oxide (DB) and antimony oxide (AO) were used as conventional fire retardant additives. Cone calorimeter experiments, UL-94, and limiting oxygen index (LOI) tests showed that the nanocomposites were superior to that of conventional flame retardant microcomposites. The flame retardant nanocomposites with DB and AO showed lower heat release rate peak and higher LOI than that of conventional fire retardant ABS microcomposites. Therefore, nanocomposites with fire retardant additives show the highest efficiency when compared with nanocomposites without additives and conventional flame retardant microcomposites, respectively.

In 2006, Ma *et al.* [28] prepared ABS/organomontmorillonite (OMT) nanocomposites and ABS/brominated epoxy resin-antimony oxide (BER-AO)/OMT nanocomposites via melt blending. In this work, OMT was modified with octadecyl trimethyl ammonium bromide by ion exchange reaction. The dispersion of OMT in

nanocomposites was investigated by WAXD and TEM. The results revealed an intercalated structure in ABS/OMT nanocomposites and the OMT layers mainly distributed in SAN phase. However, exfoliated structure was found in ABS/OMT and ABS/BER-AO/OMT nanocomposites and the OMT layers preferentially located in BER phase. The exfoliation of OMT could enhance the thermal stability of pure ABS resin and ABS/BER blends. A synergistic effect between OMT and BER-AO during the combustion of the nanocomposites was also found.

In 2006, Ma *et al.* [29] synthesized poly(4,4-diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate) (PDSPB) as a flame retardant in ABS composites. It was found that the addition of PDSPB would enhance the thermal stability and flame retardancy of ABS significantly. FTIR and SEM investigations revealed that the residual chars contained polyphosphoric or phosphoric acid, which played an important role in the process of carbonization. The chars formed from PDSPB and ABS/PDSPB composites were intact, multicellular, and strong. It was confirmed that the char structure was a critical factor for flame retardancy of ABS resin.