CHAPTER II
LITERATURE SURVEY

2.1 Layered Silicates (Clay)

2.1.1 Structure of Layered Silicates

The silicates most commonly used in nanocomposites are layered silicates (clay minerals) or phyllosilicates (rock minerals). In most cases, fine clays as cheap filler have been used in polymer nanocomposites for saving polymer consumption and reducing the composite cost.

Most clay minerals are sandwiches of two structural units, i.e., the tetrahedral and octahedral. The simplest type of sandwich is made of a single layer of silica tetrahedral with an aluminium octahedral layer on top: these are called 1:1 minerals and are of the kaolinite family. Another main type of sandwich is the 2:1 structure (smectite minerals). In smectite minerals the octahedral sites may be occupied by magnesium, iron or small metal ions as well as by aluminium. The structure of a 2:1 clay mineral (smectite) is shown in Figure 2.1
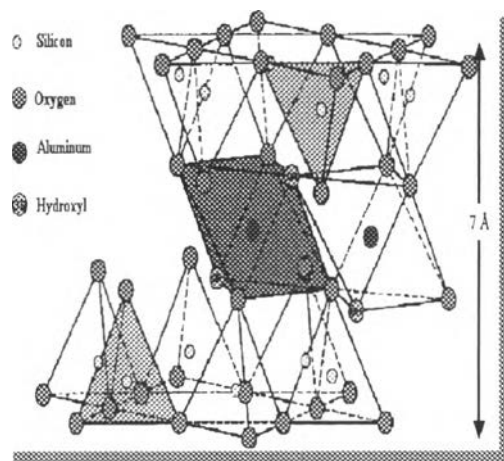

Figure 2.1 The structure of a 2:1 clay mineral (smectite minerals).

Smectite clay, shown in Figure 2.1, has the oxyanion layer consisting of an octahedral filling between two inverted silicate tetrahedral layers by sharing their apical oxygens. In a unit cell formed from 20 oxygens and 4 hydroxyl groups,

there are 8 tetrahedral sites and 6 octahedral sites along with 4 cavities surrounded by a six-membered oxygen ring on the surface. This mineral is classified as dioctahedral 2:1 phyllosilicate when two-third of octahedral sites is occupied by cation. A trioctahedral 2:1 phyllosilicate has all the octahedral sites filled with cations (Kaviratna, Pinnavaia and Schroeder, 1996; Burkett, Press and Mann, 1997). Smectite clays' ideal formulas are illustrated in Table 2.1. (Olphen, 1976)

Table 2.1 The ideal formulas of smectite clays

Mineral groups	Species	Ideal Formulas
Dioctahedral	Beidellite	$Na_x[(Al_xSi_{8-x}) Al_4O_{20}(OH)_4]$
	Montmorillonite	$Na_x[(Mg_xAl_{4-x})Si_8O_{20}(OH)_4]$
Trioctahedral	Hectorite	$Li_x[(Li_xMg_{6-x})Si_8O_{20}(OH)_4]$
	Saponite	$Na_x[(Al_xSi_{8-x}) Mg_6O_{20}(OH)_4]$

2.1.2 Properties and Modification of Layered Silicates

Montmorillonite (MMT): the clay minerals of this group make a very popular choice for nanocomposites because of their small particle size (< 2 μm) and hence polymer easily diffuses into particles. They also posses high aspect ratios (10-2000) and highly swelling capacity, which are essential for an efficient intercalation of the polymer (Wang and Pinnavaia, 1998). These are reasons for MMT-smectite clay to be selected to apply in this research.

Dai and Huang (1999) stated that clays had many attractive features in structure: active sites, such as hydroxyl groups, Lewis and Bronsted acidity; exchangeable interlayer cation; difference of SiO_4 tetrahedral sheet and $Al_2(OH)_6$ octahedral sheet in chemical stability. In addition, Giannelis (1996) and Choy *et al.* (1997) reported the stacking of the layers leading to a regular Van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers generates negative charges that are normally counterbalanced by cations residing in the interlayer space that shown in Figure 2.2. The interlayer cations are usually hydrated Na^+ or K^+, which can be exchanged with various organic cations

e.g. alkylammonium. The normally hydrophilic silicate surface becomes organophilic, as illustrated in Figure 2.3. The organic cations lower the surface energy of the silicate surface and improve wetting with most engineering plastics. The organic cations may contain various functional groups that react with the polymer to improve adhesion between the inorganic phase and the matrix.
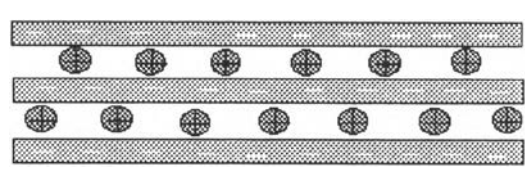

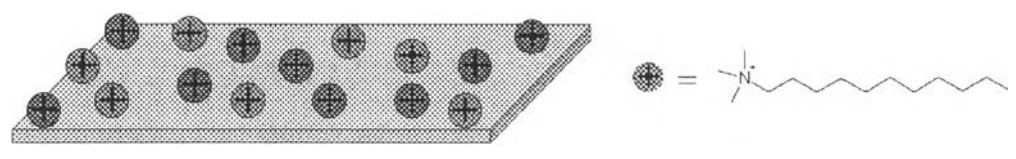**Figure 2.2** The stacks of clay platelets with counterions.

Figure 2.3 The counterions exchanged with organic cations.

Many kinds of amine bases have been studied in the modified silicate layers by intercalation into the space between silicate layers. Some researches reported the ω-amino acids having more than 11 carbon atoms stay perpendicular to the silicate layers such that an isolate silicate layer was formed in the nanocomposite (Usuki *et al.*, 1993), whereas most work focused on alkylammonium modifying agent that lays parallel to the silicate layers. Choy *et al.* (1997) studied on the dispersibility of quaternary alkylammonium modified-MMT in polar and non-polar solvents. The dispersibility of modified-MMT depends on compatibility between functional groups on the modifying agent and type of solvent. In addition, Phiriyawirut, Magaraphan and Ishida (2001) synthesized polybenzoxazine-montmorillonite nanocomposite via solvent process and found that the binary solvents having small amount of methanol showed good dispersibility. The expansion of silicate layer depended on size or molecular weight of amine modifying agent. This is as similar to primary-alkylamine and quaternary-ammonium salt

modified-MMT, the degree of basal spacing expansion was increased with the length of hydrocarbon part in the structure of modifying agents (Thaijaroen, 2000).

The crystallization rate of polyoxymethylene/MMT nanocomposite was studied. The addition of MMT, either Na-MMT or organo-MMT, may accelerate the overall non-isothermal crystallization process (Xu, Ge and He, 2001), and this is also observed in natural rubber (Thaijaroen, 2000).

2.2 Metalatranes

2.2.1 Structure of Metallatranes

Metallatranes or simply atranes are intramolecular complex cyclic ester or alkoxides of tri(2-hydroxyalkyl)amine having a skeleton of general structure I
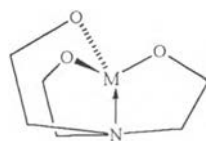
Structure I

M is an n-valent element connecting with inorganic or organic substituents when n> 3. The metallatrane term, proposed by Voronkov and Zelchan (1965), is an abbreviation used for aminotrialkoxy derivatives of different elements having the above skeleton I. For example, aminotrialkoxyphosphoranes, aminotrialkoxy-boranes and aminotrialkoxysilanes give phosephanes, boratranes and silatranes, respectively. Atrane structures are generally classified by the tricyclic model wherein a transanular M-N bond is assumed to be present.

Metallatranes with M = B, Al, Si, Ge, Sn, Pb, P, Ti, V, Mo etc. have been synthesized and studied during the last three decades (Voronkov *et al.*, 1968; Bradley *et al.*, 1978). These compounds are of interest because of their cage structure, physical/chemical properties and especially biological activity.

2.2.2 Synthesis of Alumatrane

There are several methods to prepare alumatranes. The simplest alumatrane was prepared with high yield by the reaction of aluminum alkoxide with triethanolamine (TEA) in an aromatic solvent (benzene [Mehrotra, 1962] toluene [Thomas *et al.*, 1961]) or without solvent (Icken *et al.*, 1963; Stanley 1968; Elbing *et al.*, 1964) according to Scheme 2.1.

$$n \, Al(OR)_3 \; + \; (HOCH_2CH_2)_3N \; \longrightarrow \; \left[Al(OCH_2CH_2)_3N \right]_n \; + \; 3n \, ROH \quad (2.1)$$

Triethylaluminum also reacts with TEA in toluene or hexane at $-78°C$ to form alumatrane (Higashi and Namikawa. 1967) see Scheme 2.2.

$$n \, Al(C_2H_5)_3 \; + \; n \, (HOCH_2CH_2)_3N \; \longrightarrow \; \left[Al(OCH_2CH_2)_3N \right]_n \; + \; 3n \, C_2H_6 \quad (2.2)$$

Verkade *et al.* (1993) used the alcoholysis of tris-(dimethylamido) aluminum with TEA (Scheme 2.3) and also the transligation of monomeric and dimeric alumaazatranes with TEA.

$$n \, Al(NMe_2)_3 \; + \; (HOCH_2CH_2)_3N \; \longrightarrow \; \left[Al(OCH_2CH_2)_3N \right]_n \; + \; 3MeNH \quad (2.3)$$

The starting materials to synthesize alumatrane complexes, aluminum alkoxides [Al(OR)₃] are expensive and the synthesis are multistep. Laine *et al.* (1993) have developed an inexpensive way to convert metal oxides, namely alumina and silica, into novel materials ranging from ion conducting (Chew *et al.*, 1994) liquid crystalline polymers (Laine *et al.*, 1993) to oligomeric and polymeric precursors.

Laine *et al.*, (1993) found that higher boiling point amine bases (b.p > 200°C), such as TEA and triethylenetetramine (TETA), can be used either in catalytic or stoichiometric quantities to dissolve SiO_2 Moreover, they also found

that approximately stoichiometric quantities of TEA effectively dissolve Al(OH)$_3$. The "Oxide One Pot Synthesis (OOPS) Process" for alkoxyalanes was developed after it was discovered that stoichiometric amount of TEA would dissolve aluminum hydroxide, the source material for most pure alumina (Kirk-Othermer, 1979; Cotton and Wilkinson, 1981).
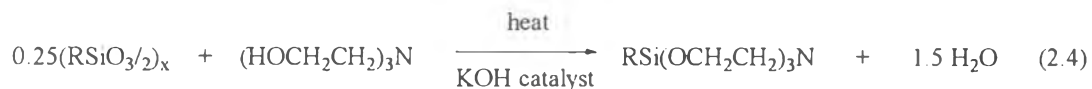
Petchsuk *et al.* (1995) synthesized alumatrane directly from Al(OH)$_3$ and TEA, and found pentamer, tetramer, trimer and the most stable species, dimer from mass spectroscopic data, ^{1}H-, ^{13}C- and ^{27}Al-NMR. Moreover, when TETA, stronger base than TEA was used, mass spectroscopic data indicated the same mixture of oligomers. Using the integral method to study the reaction kinetics, the reaction of Al(OH)$_3$ and TEA is second order overall, first order with respect to [Al(OH)$_3$] and first order with respect to [TEA]. The activation energy for this reaction was obtained using the Arrhenius' equation and it was estimated to be 62±5 kJ.mol^{-1}. Similarly to Opornsawad *et al.* (2001) synthesized alumatrane from Al(OH)$_3$ and triisopropanolamine (TRIS) via the OOPS process. Mass spectra showed the main product was pentamer bonded with TRIS that lost one H$_2$O molecule. The reaction order was again second order overall, first order with respect to [Al(OH)$_3$] and first order with respect to [TRIS]. The activation energy of this reaction was about 24±2 kJ.mol^{-1}.

2.2.3 Synthesis of Silatrane

Silatranes are 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. The first silatrane was patented by Finestone in 1960 (Punchaipetch, 1995). Finestone suggested the existance of a Si<-N transannular coordinate bond. Silatranes are interesting because of their intriguing molecular structure, biological activity and patterns of chemical reactivity.

It is known that siloxane bonds are susceptible to alcoholysis under suitable conditions. When this reaction is performed on organosilsesquioxane substrates with triethanolamines as the alcoholic reactant, the yield of silatrane is

high (Punchaipetch, 1995). Both ethyl- and phenylsilatrane were formed in high yield by this method.

$$0.25(RSiO_{3/2})_x + (HOCH_2CH_2)_3N \xrightarrow[\text{KOH catalyst}]{\text{heat}} RSi(OCH_2CH_2)_3N + 1.5 H_2O \quad (2.4)$$

It was observed qualitatively that the electron-withdrawing group on the silicon facilitates the reaction. Although KOH was employed as a catalyst in preparing the ethyl derivative, it may be unnecessary since the corresponding phenyl- and m-nitrophenylsilatranes were obtained in the absence of KOH.

In a related work (Punchaipetch, 1995), silicic acid was observed to be dissolved in excess TEA at temperature of 200°-250°C, i.e.

$$SiO_2 + TEA \xrightarrow{\text{heat}} (HOCH_2CH_2)_nN[CH_2CH_2OSi(OCH_2CH_2)_3N] + 2 H_2O \quad (2.5)$$

Punchaipetch (1995) synthesized silatrane complex directly from SiO_2 and TEA via the OOPS process. The mass spectroscopy result showed mixtures of dimer, trimer, tetramer and pentamer. The activation energy for this reaction was obtained using the Arrhenius' equation and was estimated to be 64 ± 8 kJ.mol^{-1}. The products synthesized are tractable neutral alkoxy compounds that provide novel routes to silicon containing chemical compounds, polymers, glasses and ceramics.

A parallel attempt with triisopropanolamine was unsuccessful. The silica did not dissolve and very little water was evolved even at 290°C. Verkade (1993) described similar silatrane synthesis utilizing $[(RHSiO)_{2/2}]_x$ substrates, silatrane could presumably also be obtained from the reaction of trialkyanolamine with appropriate polysilanes [i.e., $Me(MeO)_2SiSi(OMe)_2Me$] and possibly from silicon itself.

2.3 Polymer Layered Silicates (PLS)

2.3.1 Structure of Polymer Layered Silicates

There are three structurally different types of polymer layered silicate (PLS), as shown schematically in Figure 2.4. Intercalated structures are those in

which a single extended polymer chain is intercalated between the silicate host layers resulting in a well-ordered multilayer with fixed interlayer spacing. Delaminated or exfoliated structures are formed when the individual silicate layers are no longer close enough to interact with the adjacent layers' gallery cations (Lan and Pinnavaia, 1994; Giannelis, 1996). The silicate nanolayers are individually dispersed in the polymer matrix with the average distance between the segregated layers (20-200 nm) being dependent on the clay loading. The separation between the nanolayers may be regular or disordered. Exfoliate nanocomposites, show greater homogeneity than intercalated nanocomposites and so exfoliated structures posses properties that are superior to those having intercalated ones (Wang and Pinnavaia, 1998). Two types of end-tethered structures can be produced, one where the end of the polymer is attached to the outside of the silicate sheet and the other where the end of the polymer is attached to an exfoliated layer of the silicate. The second type is similar to a delaminated structure with polymer surrounding exfoliated layers of silicate.
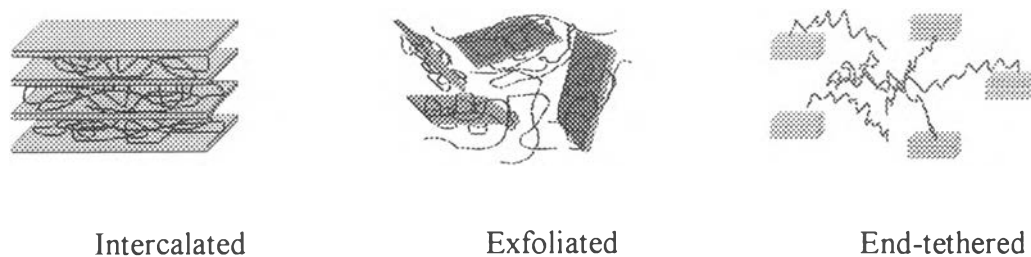

| Intercalated | Exfoliated | End-tethered |

Figure 2.4 A schematic view of polymer layered silicate structure.

2.3.2 Preparation of Polymer Layered Silicates

Nanocomposites can be formed in one of three ways, in-situ polymerization, solvent-based synthesis or melt blending synthesis. In the case of in-situ polymerization, the clay is dispersed in the monomer and the polymerization reaction is carried out. Polystyrene clay nanocomposites can be prepared by in-situ polymerization of styrene in the presence of clay (Zhu and Wilkie, 2000). Moet and Akelah (1993) achieved chemical grafting of polystyrene onto MMT interlayers by addition polymerization reactions. Messersmith and Giannelis (1995) prepared nanocomposites that were prepared by using 12-aminododecanoic acid as a

protonated host layer, followed by initiating ring-opening polymerization with ε-caprolactone monomer at 170°C for 48 h, yielding a poly(ε-caprolactone) hybrid. Similar to nylon 6-clay hybrid obtained from "One-Pot Synthesis", MMT was dispersed in water, and then ε-caprolactam, phosphoric acid and 6-aminocaproic acid as accelerator were added to the dispersion, the mixtures were reacted at 260°C for 6 h, yielding the nylon 6-clay hybrids (Kojima *et al.*, 1993).

The solvent-based synthesis involves mixing polymer solution with clay. Polyimide-clay hybrids can be prepared by dissolving clay in dimethylacetamide (DMAC) and mixing with precursor solution of polyimide, followed by removing the solvent (Yano *et al.*, 1993). Magaraphan *et al.*, (2001) used *N*-methyl-2-pyrrolidone (NMP) to dissolve clay and mixed the mixture with poly(amic acid) and 2,2-bis[4-(3,4-dicarboxyphenoxy)-phenyl]propane dianhydride (BPDA-PDA) to obtain rigid rod polyimide. Polybenzoxazine-clay nanocomposites can be obtained by this method. Phiriyawirut, Magaraphan and Ishida (2001) prepared those nanocomposites using binary solvents, dioxane and methanol to disperse clay added benzoxazine solution to gain nanocomposites.

The melt blending process involves mixing the layered silicate by annealing statically or under shear (VanderHart, Asano and Gilman, 2001), with the polymer while heating the mixture above the softening point of the polymer. During the annealing process, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers. Vaia *et al.*, (1995) and Giannelis (1996) used the "direct polymer melt" method to intercalate poly(ethylene oxide), PEO, by heating the polymer and silicate at 80°C for 6 h. Lui, Qi and Zhu (1999) studied on nylon 6/clay nanocomposites by melt-intercalation process by mixing nylon 6 with organoclay and extruding by twin-screw extruder set temperature profiles of 180°-210°-230°-220°C. Extrudate was then pelletized, dried and injected by injection molding at 220°C and 13.5 MPa. Kawasumi *et al.* (1997) also, used twin-screw extruder to produce a polypropylene nanocomposite from a modified polypropylene oligomer and modified clay. Other polymer nanocomposites comprising polystyrene (Vaia, Ishii and Giannelis, 1993), polycarbonate, polyphosphazene, polysiloxane (Burnside and Giannelis, 1995), and natural rubber can also be synthesized with this

method (Thaijaroen, 2000). Recently, unique methods to blend polymers directly with clay have employed microwaves, a latex-colloid interaction and crystallization from sol-gels (Carrado, 2000).

2.3.3 Applications of Polymer Layered Silicates

Nanocomposites can be used to improve properties of polymer, e.g. increasing mechanical properties. The Toyota research group first observed that exfoliation of layered silicates in nylon 6 greatly improved the mechanical, thermal and barrier properties of the polymer. The 5%wt layered silicate nylon 6 nanocomposites exhibited increase of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength and 126% in flexural modulus over those of pristine polymer. The heat distortion temperature showed an increase from 65° to 152°C and solvent resistance also increased while gas permeability decreased (Gilman, 1999). These composites are now used for under the bonnet applications in the automobile industry (Wang and Pinnavaia, 1998). After this success, the nanocomposite technology has been extended to other polymers—polypropylene (Kawasumi *et al.*, 1997), polyimide (Yano *et al.*, 1993; Magaraphan *et al.*, 2001) and epoxy (Wang and Pinnavaia, 1998; Lan and Pinnavaia, 1994), which showed similar results. For example, aliphatic amine-cured, epoxy nanocomposites containing 15wt% (7.5vol%) organoclay showed more than a ten-fold increase in tensile strength and modulus (Lan and Pinnavaia, 1994). The tensile strength, modulus, dielectric strength and the low water absorption of rigid-rod polyimide/MMT nanocomposites were improved with the organophilic clay content up to 3wt%, (Magaraphan *et al.*, 2001).

2.3.4 Flame Retardant Properties of Polymer Layered Silicates

The polymer-layered silicate often exhibits an increase in thermal stability, e.g. the improved thermal stability of polymethyl methacrylate (PMMA)-layered silicate nanocomposites. TGA results showed that both linear and cross-linked PMMA intercalated into Na^+-MMT have 40-50°C higher decomposition temperatures (T_d) than pure PMMA (as measured at the point of 50% mass loss).

The first mention of the potential flame retardant properties of this type of materials appeared in a 1976 Japanese patent application on nylon 6 clay nanocomposites (Gilman, 1999).

Similar results were presented involving polydimethyl siloxane (PDMS) and polyimide nanocomposites by Burside and Giannelis, 1995. PDMS-nanocomposite containing only 10% mass fraction of clay showed an increase of 140°C in T_d compared to pure PDMS elastomer (as measured at the point 50% mass loss), which normally decomposes into volatile cyclic oligomers. The permeability of PDMS also decreased dramatically, hence the increased thermal stability was attributed to hinder diffusion of volatile decomposition products within the nanocomposite. Superior thermal behavior was observed for rigid-rod polyimide with low thermal expansion coefficient, high glass transition and yielding temperatures (Magaraphan et al., 2001). Recently, Bourbigot, Devaux and Flambard (2002) studied the flammability of polyamide-6/clay nanocomposite as textile fabrics. Heat releasing rate of PA-6/nanocomposites was reduced by 40% in comparison with pure PA-6.

2.4 Burning of Plastics (Becker et al., 1990)

2.4.1 The Combustion Process

The combustion of plastics is a process comprising many steps, some of which are still uninvestigated. It therefore cannot be described quantitatively, although it is possible to describe it qualitatively. A simplified schematic representation of the various phenomena, which take place during the combustion of plastics, is shown in Figure 2.5. The three essential stages required to initiate the combustion are heating, thermal decomposition or pyrolysis and ignition. Ignition is normally caused by the presence of an external heat source, such as a flame or a spark or, if the temperature is high enough, it occurs spontaneously.
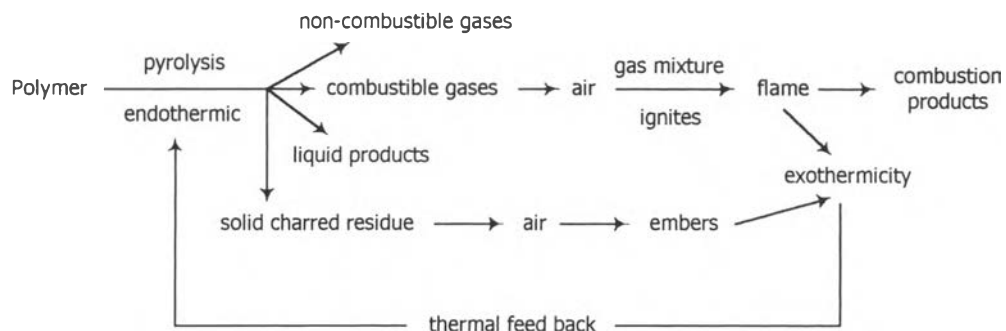
Figure 2.5 The polymer combustion process.

2.4.2 Flame Spread

The rate of pyrolysis will be accelerated leading to an increasing supply of fuel to the flame, which then spreading over the polymer surface. As a simplified model of the flame chemistry, reactions occur in hydrocarbon diffusion flame. The important step is the chain branching step propagated by the highly reactive H• and OH• radicals. High velocity on the flame front results in rapid flame spread. In case of the OH• radicals, their avalanche-like proliferation can be illustrated by the combustion of ethane, as shown in Figure 2.6. It should be remembered that the H• radicals would also make a similar contribution.
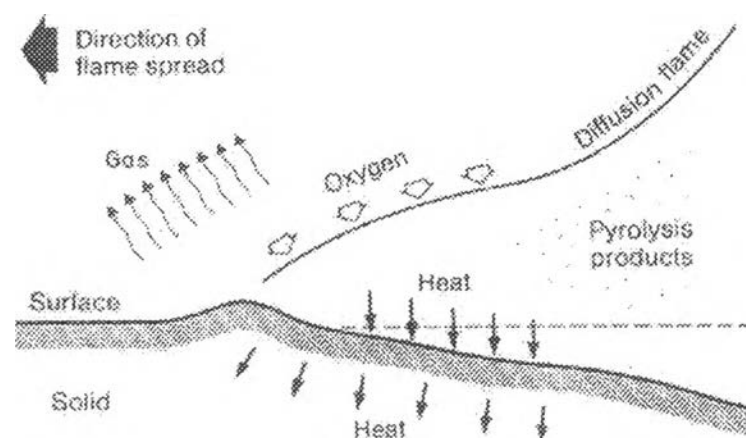

Figure 2.6 The combustion of ethane and free radical generation.

According to more recent investigations, the H• radicals appear to be at least as important as the OH• radicals are. A phenomenological description of flame spread along a polymer surface is given in Figure 2.7. The diffusion flame advances over the decomposed polymer surface. As with the candle flame, the surface temperature of the polymer (500°C) is lower than that of the diffusion flame and of the edge of the flame, where reaction with oxygen occurs (1200°C).

Figure 2.7 A schematic of flame spread
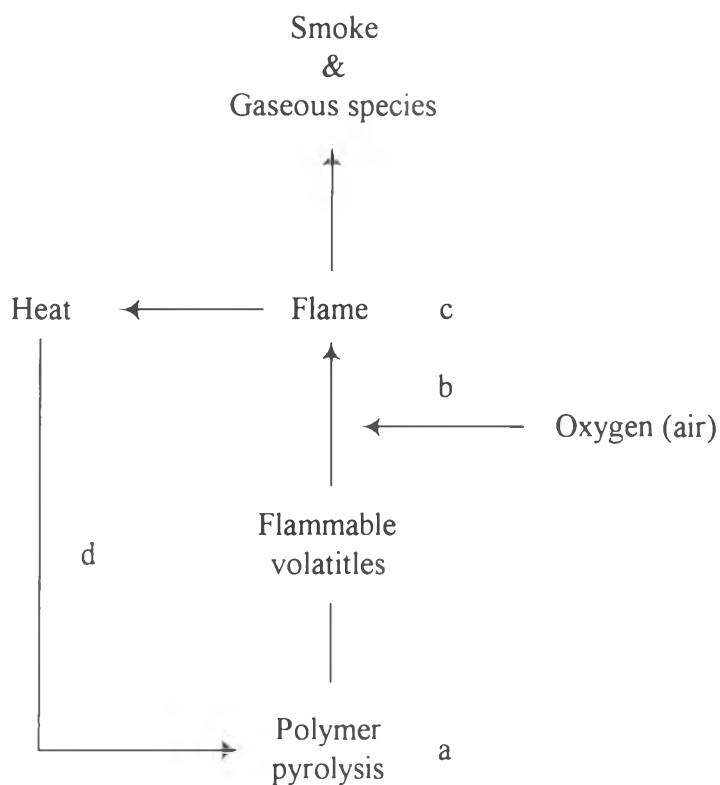
2.5 Flame Retardation

Figure 2.8 The self-sustaining polymer combustion cycle; a-d represent potential modes of flame retardant action.

A simple schematic representation of the self-sustaining polymer combustion cycle is shown in Figure 2.8. Flame retardants act to break this cycle, and thus extinguish the flame or reduce the burning rate, in a number of possible ways:

• By reducing the heat evolved to below that required sustaining combustion.

• By modifying the pyrolysis process to reduce the amount of flammable volatile evolved in favor of increasing the formation of less flammable char, which also acts as a barrier between the polymer and the flame (a).

• By isolating the flame from the oxygen/air supply (b).

• By introducing into the plastic formulation compounds, which will release chlorine or bromine atoms if, the polymer is heated to near the ignition

temperature. Chlorine and particularly bromine atoms are very efficient flame retardant inhibitor (c).

- By reducing the heat flow back to the polymer to prevent further pyrolysis. This can be achieved by the introduction of a heat sink, e.g. aluminium oxide trihydrate (ATH, $Al(OH)_3$) which decomposes endothermically or by arranging a barrier, e.g. char or intumescent coating, when the polymer is exposed to fire conditions (d).

- By developing inherently flame retarded polymer systems.

Most flame retardant systems in use today have been developed empirically. Current interest in obtaining a better understanding of polymer combustion and interaction of flame retardants therewith is motivated by the requirement to develop environmentally friendly flame retardant systems with enhanced performance. Thus, layered silicates and inorganic flame retardant have been attractive materials to act as flame retardants for polymers in this research.