CHAPTER 1

INTRODUCTION

1.1 SIGNIFICANCE OF FLAME RETARDATION IN POLYMERS

Over the last few decades the world has witnessed spectacular growth and development in the use of polymeric materials in day-to-day life, industry and high performance applications. Production of polymers by volume has exceeded over that of steel and aluminium. They have successfully substituted advanced metals and ceramics in certain high performance applications and a host of polymers with unprecedent properties are emerging from advances in new methods of synthesis and processing. Although these developments have revolutionised the world of materials, polymers with the exception of a few are susceptible to deterioration on exposure to heat and flame. Fires have been reported to be one of the principal scourges of mankind and today with the increasing use of polymeric materials, this problem has aggravated to the extent of worldwide concern for improved protection for property and human life. The use of flame retardants for the control of the flammability of materials of organic origin dates back even to early Egyptian civilization, but only recently, search for newer and better flame retardants that fulfil the standards set for fire prevention and control and also for a better understanding of the mechanism and behaviour of flame retardants so that the existing ones could be improved upon, has
begun on a systematic and scientific way.

1.2 HISTORICAL DEVELOPMENT OF FLAME RETARDANTS

It was Gay-Lussac [1] who initiated for the first time in France in 1821 basic scientific investigation on flame retardants. He noted that the ammonium salts of sulfuric, hydrochloric and phosphoric acids were very effective fire retardants on hemp and linen and that the effect could be improved considerably by using mixtures of ammonium chloride, ammonium phosphate and borax. Thus the basic elements of modern fire retardant chemistry were defined early in recorded history and remained the state of the art until early in the twentieth century. The early historical developments [1-5] are listed in Table 1.1.

The demands of the armed forces in World War II for a fire-retardant waterproof treatment for canvas tenting led to the development of a combination treatment containing a chlorinated paraffin (CP), antimony oxide, and a binder [6,7]. This was the first use of the halogen-antimony synergistic combination treatment that has since proven so effective in many fire-retardant polymer products and marked the introduction of organic halogen compounds in place of inorganic salts previously in vogue. Even though this new treatment was found to be useful in PVC both as a fire retardant and plasticizer additive, it tended to 'wash out' in many environments in which PVC was used. This deficiency of CP led to the conclusion that a reactive fire-retardant
system would be preferred, something which would be chemically reacted into the polymer at some stage of the synthesis and/or fabrication of the final product and confer permanent fire-retardant properties on the final product.

Table 1.1: Early historical fire retardant developments

<table>
<thead>
<tr>
<th>Development</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum used by Egyptians to reduce the flammability of wood</td>
<td>About 450 BC</td>
</tr>
<tr>
<td>Romans used a mixture of alum and Vinegar on wood</td>
<td>About 200 BC</td>
</tr>
<tr>
<td>Mixture of clay and gypsum used to reduce flammability of theater curtains</td>
<td>1638</td>
</tr>
<tr>
<td>Mixture of alum, ferrous sulphate and borax used on wood and textiles by Wyld in great Britain</td>
<td>1735</td>
</tr>
<tr>
<td>Alum used to reduce flammability of balloons</td>
<td>1783</td>
</tr>
<tr>
<td>Gay-Lussac reported a mixture of (NH₄)₃PO₄, NH₄Cl and borax to be effective on linen and hemp</td>
<td>1821</td>
</tr>
<tr>
<td>Perkin described a FR treatment for cotton using a mixture of sodium stannate and ammonium sulphate</td>
<td>1913</td>
</tr>
</tbody>
</table>
The first fire-retardant polyester containing a reactive fire retardant monomer was introduced by the Hooker Electrochemical Corporation in the early 1950s. It contained chlorendic acid (I) as the reactive monomer [8] as shown in Fig. 1.1.

![Fig. 1.1](image)

This pioneering development led rapidly to the introduction of various reactive halogen and phosphorus containing monomers, such as tetrabromophthalic anhydride, chlorostyrene and tetrabromobisphenol A, which found application in a wide variety of condensation polymer systems.

The next major development resulted from the need for an acceptable fire-retardant system for such new thermoplastics as polyethylene, polypropylene, and nylon. The use of a reactive monomer was not applicable to these polymers because the crystallinity upon which their desirable properties depended was reduced or destroyed by adding the fire-retardant. The
introduction of inert fire retardant fillers in 1965 defined two novel approaches to fire-retardant polymers. One of these products was a thermally stable insoluble chlorocarbon prepared from cyclooctadiene and hexachlorocyclopentadiene. The extreme insolubility of this high-melting thermally stable hydrocarbon allowed it to be compounded into most thermoplastics without decomposition or discoloration. The other fire-retardant filler, hydrated aluminium oxide (or alumina) [9] exerts its fire-retardant effect in polymer compositions by dehydrating under flame conditions. Because of its relatively low decomposition temperature (245-320°C) hydrated alumina is most useful in polymer compositions requiring low processing temperatures such as unsaturated polyesters. The major advantages of this fire retardant system are low smoke production and the fact that no hydrogen halide off-gases are produced during pyrolysis on fire exposure. These developments can be summarised as follows (Table 1.2).

Table 1.2: Most important modern developments in polymer fire-retardance

<table>
<thead>
<tr>
<th>Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorinated paraffin, antimony oxide and a binder as a treatment on canvas</td>
</tr>
<tr>
<td>Reactive fire retardants, chlorine containing unsaturated polyesters</td>
</tr>
<tr>
<td>Filler-like fire retardants</td>
</tr>
<tr>
<td>Oxygen Index method of evaluating relative polymer flammability</td>
</tr>
<tr>
<td>Intumescent fire-retardant systems</td>
</tr>
<tr>
<td>Inherently fire-retardant polymers</td>
</tr>
<tr>
<td>Wide-spectrum flame retardants</td>
</tr>
</tbody>
</table>
1.3 THE COMBUSTION OF POLYMERS

Since the action of FRs is to interfere in some step in the burning process of polymers [10], a brief discussion is here included on the combustion of polymers [11-23]. The combustion of polymers takes place in three stages involving a heating phase, a thermal pyrolysis stage and ignition [13,14]. The heating phase primarily depends on the relative flux and temperature of heat source. In the case of thermoplastics which melt during heating, the melt flowing away (dripping) from the heating source gives an apparently erroneous conclusion regarding resistance to flame. The flammability of a material is largely determined by the pyrolysis stage when a pyrolytic decomposition prior to ignition occurs with the elimination of gaseous products. The composition of the gaseous products determines primarily the flammability of the material. Ignition occurs when the gaseous products forming a mixture with oxygen in the air exceed the flammability limits. In fact a triad of fuel, air (oxygen) and heat has to be established to ensure burning to occur. The process of combustion can be represented in Fig.1.1.

The thermal feedback maintains the combustion process upon a continued supply of oxygen from the surrounding atmosphere.
Fig. 1.2: Process of combustion of an organic polymer

$Q_1$, $Q_2$ = heat
1.4 THE MECHANISM OF FLAME RETARDANCY

The flame retardant may act in the condensed phase by altering the thermal breakdown of the polymer in such a way that either the nature or the rate of evolution of the gaseous decomposition products is changed. As a consequence when these products mix with the oxidant, the composition of the resulting mixture no longer lies within the flammable range \([4,7,24-26]\). It can also act in the gaseous phase, the flame retardant may dissociate into free-radical acceptors which react with the chain-propagating radicals of the combustion \([4,7,24-26]\). A combination of these two mechanisms is also possible.

1.4.1 The mode of action of phosphorus flame retardants

Condensed phase mechanism

The behaviour of phosphorus based flame retardants has been studied extensively, but primarily in cellulose. The most generally accepted mechanism for phosphorus fire retardancy in cellulose is the condensed phase mechanism. The flame retardant is converted by thermal decomposition to phosphoric acid which alters the mechanism of decomposition of the cellulose in the condensed phase so that the principal products are carbonaceous char rather than levoglucosan and other flammable compounds \([4,7,24-28]\). The formation of char involves catalytic dehydration of the hydroxyl groups, esterification by the polyphosphoric acid formed and finally cross-linking and skeletal rearrangement \([29]\).
The generation of phosphoric acid is most easily explained as resulting from the well known decomposition of the alkyl phosphorus ester, to an olefin and the corresponding acid [29]. This reaction together with the postulated char forming dehydration of the cellulose is depicted in the following reactions:

Ester decomposition

\[
R-CH_2-CH_2-O-P^- \xrightarrow{\Delta} R-CH = CH_2 + HO-P^- \quad (1)
\]

\[
2 \text{HO-P}^- \xrightarrow{\Delta} \text{P}^-\text{O-P}^- + \text{H}_2\text{O} \quad (2)
\]

Esterification and dehydration

\[
\text{-CH}_2\text{-CH}_2\text{OH} + \text{P}^-\text{O-P}^- \rightarrow \text{CH}_2\text{-CH}_2\text{O-P}^- + \text{P}^-\text{OH} \quad (3)
\]

\[
\text{-CH}_2\text{-CH}_2\text{O-P}^- \rightarrow \text{-CH} = \text{CH}_2 + \text{P}^-\text{OH} \rightarrow \text{char} \quad (4)
\]

A second possibility of forming unsaturated compounds with subsequent charring is the acid-catalysed elimination of water from the cellulose:

\[
R-\text{CH}_2\text{-CH}_2\text{-OH} \xrightarrow{\text{H}^+} R-\text{CH}_2\text{-CH}_2\text{OH}^+ \xrightarrow{\cdot} R-\text{CH} = \text{CH}_2 + \text{H}_2\text{O} + \text{H}^+ \quad (5)
\]
The existence of a condensed phase mechanism is supported by the fact that all phosphorus compounds that are capable of decomposing to acid fragments are effective fire retardants for cellulose whereas fully neutralised salts of nonvolatile metals are not [29,30]. Addition of as little as 1.0% of phosphorus to cellulose causes a several fold increase in char yield under flame conditions [31]. Also the phosphorus from the fire retardant is found to be largely or completely retained in the residual char [32].

The high efficiency of phosphorus fire retardants in polyurethane (Pu) foams has also been suggested to be the result of acidic degradation products which then promote the formation of a structurally stable insulating char [33,34]. Similar condensed phase mechanism has also been proposed in the case of other hydroxylated or oxygenated polymers like epoxy resins [35-36] and polymethyl methacrylate (PMMA) [37].

In the case of non-oxygenated polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) etc. the acid catalysed char forming mode of action of phosphorus plays a less evident role and in fact phosphorus is not so effective in such polymer systems as it is in oxygenated polymers [38-40]. The flame retardant effect observed in these cases has been attributed to the formation of polyphosphoric acid which acts as a physical barrier to passage of heat, oxygen or fuel [38-40]. Savides et al [41] also have presented evidence for a condensed phase mode
of action involving char coating for phosphorus flame retardants in PP.

Gaseous phase mechanism

Considerable attention has been directed in recent years to a possible gaseous phase mechanism of action of phosphorus flame retardants [38-40]. Volatile phosphorus compounds have been shown to be some of the most efficient gas phase inhibitors in premixed flames [42-44]. Lask and Wagner have shown that trimethylphosphate is three times more effective as bromine in inhibiting a stoichiometric premixed n-hexane flame [43]. Hastie [45] and Granzow [44] have reported that compounds such as triphenylphosphine oxide break down in the flame as shown below to give small molecular species such as PO. The rate controlling hydrogen atom concentration in the flame was shown spectroscopically to be greatly reduced,

\[
\begin{align*}
(C_6H_5)_3PO & \rightarrow \text{PO, P, and P}_2 \\
H + PO + M & \rightarrow \text{HPO + M} \\
OH + PO & \rightarrow \text{HPO + O} \\
\text{HPO} + H & \rightarrow \text{H}_2 + \text{PO}
\end{align*}
\]

when the phosphorus species were present [45]. The mechanism proposed for flame retardancy in this situation is scavenging of
by phosphorus radicals such as PO and thus reducing the energy of the flame [45].

The existence of gaseous phase mechanism for phosphorus compounds has been reported only in the case of a few polymer systems [46-48] compared to condensed-phase mechanism. In some cases, a combination of these two mechanisms is also possible [46-48]. A vapour phase physical shielding has been postulated for tris(dibromopropyl) phosphate in polypropylene [46]. When certain polyester cotton blends having built-in phosphorus, in the form of phosphine oxide structure is burned, it has been found that part of the phosphorus is volatilized and part is retained in the char, thus suggesting the possibility of both the mechanisms [47,48].

Thermally stable but low boiling esters like triphenyl phosphate and tricresyl phosphate are found to induce no char in cellulose [49], PMMA [50] etc. The flame retardancy observed in these cases has been attributed to a gaseous phase mechanism [49,50]. These compounds may be acting in the same way as reported in the case of triphenyl phosphine oxide. However, it has been found that these compounds are less effective as flame retardants compared to compounds which give rise to phosphoric acid and act in the condensed phase [49,50]. Similarly, triphenyl phosphine oxide which acts in the gaseous phase is found to be less efficient compared to phosphoric acid which acts in the condensed phase in flame retarding polyethylene terephthalate [51].
Thus it can be seen that the mechanism by which phosphorus compounds act in flame retardation depends on the structure of the flame retardant as well as the nature of the substrate polymer.

1.4.2 Mechanism of action of halogen flame retardants

The halogenated flame retardants are generally considered to act through suppression of the gas phase radical reactions \[29,52,53\]. The very high energy OH and H formed by chain branching

\[
\begin{align*}
\cdot H + O_2 & \longrightarrow OH + \cdot O \\
\cdot O + H_2 & \longrightarrow OH + \cdot H 
\end{align*}
\]

are removed by the halogen containing flame retardant. At first the flame retardant breaks down into

\[
R - x \longrightarrow \cdot R + \cdot x
\]

The halogen radicals react to form a hydrogen halide.

\[
\cdot A + RH \longrightarrow \cdot R + HX
\]

which in turn interfere with the free radical mechanism

\[
HX + \cdot H \longrightarrow \cdot H_2 + \cdot X
\]

\[
HX + \cdot OH \longrightarrow \cdot H_2O + \cdot X
\]
Thus the high energy H and OH radicals are removed by the reaction with HX and replaced with the lower energy X radicals. The hydrogen halide consumed is regenerated by reaction with hydrocarbon so that the inhibition reaction can take place again.

Hindersinn and Witschard suggest that halogen containing flame retardants are also effective in the condensed phase [29]. Thus HBr acts as an oxidative catalyst, forming oxidized products with a tendency to cyclize and condense to yield carbonaceous products [29].

1.5 FLAMMABILITY TESTS AND TERMINOLOGY

Laboratory screening tests have been most generally used in fire retardant research. These screening tests or small scale tests compare burning rates of various plastics [54]. Such tests as D 635-74, flammability of rigid plastics, and D 1692-74, flammability of plastic foams and sheeting, fall into this category. ASTM E-84 tunnel test is the most common design for materials. Since it attempts to classify materials under actual use conditions, it requires large samples and extensive test equipment. Two most commonly used small scale tests are the Limiting Oxygen Index test and the Underwriter's Laboratory vertical flame test.

1.5.1 Limiting oxygen index

The LOI test was first developed by Fenimore and Martin in 1966 [55] from an idea originally proposed by Simmons and Wolfhard for gaseous and liquid fuels [56]. Oxygen index is
not an ignition test but rather a test for measuring propagation and extinction related phenomena [57]. The LOI is the minimum percentage of oxygen in an oxygen-nitrogen atmosphere required to sustain combustion of a material after ignition and can be represented as follows:

\[
\text{LOI} = \frac{[O_2] \times 100}{[O_2] + [N_2]}
\]

Two of the reasons for the wide acceptance of this method are its precision and reproducibility of the results obtained by different workers in different laboratories. Table 1.3 gives the LOI values for various polymers.

1.5.2 Underwriter's Laboratory vertical flame test

In the UL-94 vertical burn test specimens are 6 in. in length by 1/2 in. in width by either 1/4, 1/8 or 1/16 in. in thickness. Conditions during the test are more severe with a 1/16 in. thick specimen than with thicker test specimens. The specimen is clamped vertically and a blue Bunsen burner flame applied to the bottom end of the specimen for a period of 10 sec and then removed and the duration of combustion is noted. If combustion ceases within 36 sec. after removal of the burner flame, the burner flame is again placed under the specimen for 10 sec. immediately after the combustion stops. The burner flame is again withdrawn and the duration of combustion again noted.
Table 1.3: LOI values of polymers

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Polymer</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Polymethylene oxide</td>
<td>15</td>
</tr>
<tr>
<td>2.</td>
<td>Polyethylene oxide</td>
<td>15</td>
</tr>
<tr>
<td>3.</td>
<td>Polyethylene</td>
<td>18</td>
</tr>
<tr>
<td>4.</td>
<td>Polypropylene</td>
<td>18</td>
</tr>
<tr>
<td>5.</td>
<td>Polystyrene</td>
<td>18</td>
</tr>
<tr>
<td>6.</td>
<td>Polyisoprene (natural rubber)</td>
<td>18</td>
</tr>
<tr>
<td>7.</td>
<td>Polymethyl methacrylate</td>
<td>18</td>
</tr>
<tr>
<td>8.</td>
<td>Cellulose</td>
<td>18</td>
</tr>
<tr>
<td>9.</td>
<td>Polybutadiene</td>
<td>18</td>
</tr>
<tr>
<td>10.</td>
<td>Cellulose acetate</td>
<td>19</td>
</tr>
<tr>
<td>11.</td>
<td>ABS</td>
<td>19</td>
</tr>
<tr>
<td>12.</td>
<td>Epoxy</td>
<td>20</td>
</tr>
<tr>
<td>13.</td>
<td>Polycrylonitrile</td>
<td>20</td>
</tr>
<tr>
<td>14.</td>
<td>Poly vinyl carbazole</td>
<td>22</td>
</tr>
<tr>
<td>15.</td>
<td>Poly vinyl alcohol</td>
<td>23</td>
</tr>
<tr>
<td>16.</td>
<td>Poly vinyl fluoride</td>
<td>23</td>
</tr>
<tr>
<td>17.</td>
<td>Chlorinated polyether</td>
<td>23</td>
</tr>
<tr>
<td>18.</td>
<td>Poly 3,3-bis(chloro methyl)-1,3 epoxy alkane</td>
<td>23</td>
</tr>
<tr>
<td>19.</td>
<td>Nylon 6</td>
<td>24</td>
</tr>
<tr>
<td>20.</td>
<td>Nylon 6,6</td>
<td>24</td>
</tr>
<tr>
<td>21.</td>
<td>Poly ethylene terephthalate</td>
<td>25</td>
</tr>
<tr>
<td>S.No.</td>
<td>Polymer</td>
<td>LOI</td>
</tr>
<tr>
<td>------</td>
<td>------------------------------------------------------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>22.</td>
<td>Wool</td>
<td>25</td>
</tr>
<tr>
<td>23.</td>
<td>Polychloroprene</td>
<td>26</td>
</tr>
<tr>
<td>24.</td>
<td>Poly carbonate</td>
<td>27</td>
</tr>
<tr>
<td>25.</td>
<td>Polyphenylene oxide</td>
<td>29</td>
</tr>
<tr>
<td>26.</td>
<td>Poly-m-phenylene isophthalamide</td>
<td>29</td>
</tr>
<tr>
<td>27.</td>
<td>Silicone rubber</td>
<td>30</td>
</tr>
<tr>
<td>28.</td>
<td>Chlorinated modacrylics (vinyl chloride acrylonitrile copolymers)</td>
<td>30</td>
</tr>
<tr>
<td>29.</td>
<td>Poly arylene sulfones</td>
<td>30</td>
</tr>
<tr>
<td>30.</td>
<td>Poly(2,6-dimethyl) phenylene oxide</td>
<td>31</td>
</tr>
<tr>
<td>31.</td>
<td>Poly furfuryl alcohol</td>
<td>31</td>
</tr>
<tr>
<td>32.</td>
<td>Poly(2,6-diphenyl phenylene oxide)</td>
<td>34</td>
</tr>
<tr>
<td>33.</td>
<td>Polyarylate</td>
<td>34</td>
</tr>
<tr>
<td>34.</td>
<td>Phenolic resin</td>
<td>35</td>
</tr>
<tr>
<td>35.</td>
<td>Poly-bisphenol terephthalate</td>
<td>38</td>
</tr>
<tr>
<td>36.</td>
<td>Polyether sulfone</td>
<td>38</td>
</tr>
<tr>
<td>37.</td>
<td>Polyether ether ketone</td>
<td>40</td>
</tr>
<tr>
<td>38.</td>
<td>Polyvinyl chloride</td>
<td>42</td>
</tr>
<tr>
<td>39.</td>
<td>Polyamide-imide</td>
<td>43</td>
</tr>
<tr>
<td>40.</td>
<td>Polyphenylene sulphide</td>
<td>44</td>
</tr>
<tr>
<td>41.</td>
<td>Polyvinylidene fluoride</td>
<td>44</td>
</tr>
<tr>
<td>42.</td>
<td>Polyether-imide</td>
<td>47</td>
</tr>
<tr>
<td>43.</td>
<td>Polybenzimidazole</td>
<td>48</td>
</tr>
<tr>
<td>44.</td>
<td>Polypyrromellitimide</td>
<td>50</td>
</tr>
<tr>
<td>Sl.No.</td>
<td>Polymer</td>
<td>LOI</td>
</tr>
<tr>
<td>-------</td>
<td>--------------------------------------------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>45.</td>
<td>Polyvinylidene chloride</td>
<td>60</td>
</tr>
<tr>
<td>46.</td>
<td>Polyethylene-CO-chlorotrifluoroethylene</td>
<td>60</td>
</tr>
<tr>
<td>47.</td>
<td>Carbon</td>
<td>60</td>
</tr>
<tr>
<td>48.</td>
<td>Polychlorotrifluoroethylene</td>
<td>95</td>
</tr>
<tr>
<td>49.</td>
<td>Polyether fluoroethylene</td>
<td>95</td>
</tr>
</tbody>
</table>
The rating of test specimens in the UL-94 test are as follows. V-O if combustion stops within 5 sec. and does not drip flaming particles V-1 if combustion stops within 25 sec. and does not drip flaming particles, and V-11 if combustion stops within 25 sec. but releases flaming particles or drips during that time. Specimens in which the combustion does not stop are categorized as nonrated (N.R.). Apart from these parameters, ignition delay [58-61] and burning rate [62-66] are also used to characterize combustion of polymers.

1.6 METHODS OF FLAME RETARDATION

The general methods that are applied to achieve flame retardancy in polymeric materials can be grouped in four major headings [26,67].

(a) Chemical methods involve use of appropriate chemical compounds or elements which function by modifying either the condensed phase or vapour phase processes. The chemical methods will involve any of the following modifications:

i. Use of flame retardant additive in the polymer. They are added prior to or during some step in fabrication. They must be stable under the conditions of fabrications and is the most widely used method particularly for polyester resins, epoxy resins, polyurethane foams etc.
ii. Copolymerisation with a fire retardant comonomer to get a block or graft copolymer. This is advantageous in the sense that the flame retardant becomes integral part of the polymer. Graft copolymerisation is emerging as a useful method.

iii. Use of reactive additive that can be chemically bonded to the polymer so that it is permanently fixed.

iv. Blending with other flame retardant polymers.

(b) The gas generation method uses FRs to produce non-combustible gases that dilute the fuel-oxygen mixture below the flammability limits.

(c) The coating methods provide a fire-retardant coating which insulates the substrate from contact with further heat and fuel-air mixtures. Intumescent coatings are noteworthy here because of their applicability and is practical in wood, cotton, wool etc. [68,69]. They are systems that puff up to produce foams that insulate the substrate and protect it from heat.

(d) The thermal techniques trigger components of the solid to consume by an endothermic process so that the heat generated during the pyrolysis cools the system below the ignition point [70]. Thus addition of FRs can raise the decomposition temperature of the polymer through
for example crosslinking, reduce the fuel content of the chain scission and promote dripping, induce selective decomposition pathways such as reactions that lead to thermally stable structures (eg. char) or prevent heat/oxygen by mechanical means from reaching the pyrolysis site (eg. coating).

1.7 ADDITIVITY, SYNERGISM AND ANTAGONISM IN FLAME RETARDANCY [27]

Combinations of flame retardants may be said to have additive, synergistic or antagonistic effects. An additive effect is the sum of the effects of the two components taken independently. A synergistic effect is an observed effect greater than the additive effect, and an antagonistic effect is one which is less than an additive effect.

Critical review of specific interactions:

1.7.1 Halogens with antimony

The interaction of antimony most commonly as antimony oxide with halogenated polymers or polymers containing halogenated additives is the classic case of flame-retardant synergism. The area of inorganic antimony compounds and certain other heavy-metal compounds as flame-retardant synergists with halogen donors has been thoroughly reviewed by J.J. Pitts [71].

In a number of systems reviewed by Pitts, the flame-
retardant effect of antimony oxide has been shown to increase as halogen is added to the system up to an atomic ratio of three halogen atoms per antimony atom. Antimony halides have been shown to be potent flame repressants when directly volatilized into a gas flame. Therefore converging evidence points to the basis of the antimony-halogen synergism is being the formation of volatile flame-retardant SbCl₃ or SbBr₃.

1.7.2 Interaction of antimony and phosphorus

Scattered reports have appeared in the literature to the effect that less than additive or even antagonistic results may be obtained in some systems with combinations of phosphorus and antimony flame retardants. Fenimore [72] reported that the oxygen index of polyethylene containing both halogen and phosphorus was not increased by added Sb₂O₃. Significantly, he reported that the antimony was not vaporized when the compositions burn. He hypothesized that phosphorus prevents the antimony-halogen synergism by preventing the vaporization of antimony.

1.7.3 Phosphorus-halogen interactions

Although the concept of a phosphorus-halogen synergism appears to have gained some currency as a result of its repetition in a number of reviews, it will be shown that evidence for the reality of this supposed phenomenon is dubious.

Piechota [34] conducted a thorough study of the effect
of P-, Br-, and Cl-containing flame retardants, separately and in combination, in rigid urethane foams and found that there is no P-Br synergism but additive effect exists. Hindersinn [73] in his studies on phosphorus-halogen interactions in polyester resins indicated that a small but definite synergism exist between phosphorus and chlorine in the system.

The formulation of phosphorus halides and oxyhalides from phosphorus additives and halogen donors has been postulated probably by analogy with the antimony-halogen case and the phosphorus-halogen compounds have been considered to be either free-radical quenchers or flame retardants in some way [74].

1.7.4 Nitrogen-phosphorus interactions

Nitrogen-phosphorus synergism appears real in cellulose [75-77], but its occurrence and magnitude show a subtle dependence on the detailed structure of the nitrogen compound and even on the mode of application. The catalysis of cellulose phosphorylation by the nitrogen compound appears to be involved [75-77]. Many reports of synergism are of dubious significance because the effect is not well defined in reference to an additive model.

1.8 PROBLEMS IN FLAME-RETARDANT APPLICATION

There are many problems related to flame retardant applications in polymers. Though lot of research and developmental
work have gone into solving these problems, some of them still remain potential areas of intense study.

One of the earlier problems when water soluble inorganic salts were used as flame retardants was the tendency of leachability which with the introduction of organic was partially solved. However, low molecular weight organic flame retardants bloom causing much discomfort to the user. Also addition of large amounts of fire retardants are required in many cases and this tells upon the performance properties of the polymer and may cause deleterious effects of the flame retardants. The incorporation of effective amounts of flame retardants in polymers without impairing polymer properties is an extremely difficult problem [67].

The problem of retention of flame retardant activity throughout the life of a polymer has given rise to a lot of studies regarding the evaluation of the effect of environmental conditions which the product is likely to encounter in use (e.g. light, temperature, abrasion, humidity, reactive gases and liquids etc.) [67]. The organic compounds of phosphorus and halogen are well known and can cause environmental hazards and pollution [78-80].

There are also problems concerned with compatibility and miscibility with various polymers. The evolution of smoke and toxic gases poses a major problem for flame retardant technologies. Another problem that is currently gaining interest is
the combustion toxicity of polymers [81,82] which possibly needs appropriate definition and test methods for evaluation [83]. Another major concern is the added cost that comes with the addition of a new material.

1.9 WIDE SPECTRUM FLAME RETARDANTS

The literature on FRs is replete with innumerable examples for various applications, but there is no FR that satisfies all the requirements. For each application a separate flame retardant has to be selected, that too based on the nature of the polymer and its properties. This increases the complexity in FR development and evaluation. Attention towards the development of a wide spectrum FR that satisfies most of the FR requirements and at the same time compatible with a broad range of polymers has increased.

Recent developments indicate increased use of FRs containing more than one FR element in the same molecule [84]. There are indications that if the FR elements particularly Br is distributed between aromatic and aliphatic segments of the same molecule the FR effectiveness increases [85]. There is also a recent report [86] that the presence of aliphatic segments attached to the aromatic portion increases flame retardancy particularly Br attached to the aliphatic portion of such a molecule. Consider that such a molecule is an amphibilic system having both hydrophilic and hydrophobic moiety. Such a system is expected to be compatible and miscible with a wide range of polymers. This gives rise to
possibilities for developing wide spectrum FRs. There are a variety of such amphibilic molecules existing in nature. One example is cardanol, obtained from the plant Anacardium occidentale L. as a byproduct of the cashew industry [87]. Such molecules have potentialities for chemical modifications to introduce FR groups and also have functional sites for polymerisation into polymeric FRs [88]. Since a higher loading of FR is needed in the case of polymeric FRs [27] the optimum way is to oligomerise them into prepolyomers. Such prepolyomers will have the advantage of being non-blooming because of higher viscosity than the conventional FRs. It is also not expected to affect deleteriously mechanical properties of the polymers compared to conventional FR chemicals. The availability of functional sites can be utilised to prepare reactive prepolyomers that could be used to modify the polymer. Since the system is still in liquid nature processing is easier. In fact most of the drawbacks enlisted from conventional FRs could be overcome by the prepolymer techniques.

1.10 FLAME RETARDANT COMPOUNDS

Lewin et al [26] and Tesoro [67] identify an ideal FR as follows: (1) it should reduce flammability to a given standard, (2) reduce (or at least not to increase) smoke generation, (3) not to increase toxic products, (4) be retained in the product through normal life, (5) have accepted minimal deleterious effect on the performance properties of the polymer, (6) should be compatible with the polymer, and (7) should not cause economic penalty.
In general, compounds of the elements P, N, halogens, boron, antimony and salts of a few other metals are found to exhibit FR characteristics [7]. Based on their mechanism of action flame retardants can be classified as follows [7,26,27,67]: (1) chain transfer agents which slow down the free radical chain reactions in the gaseous phase e.g. organic compounds of halogens, (2) materials that act as char formers e.g. inorganic acids and salts that act as dehydrating agents and organic compounds of phosphorus that contribute to the solid phase mechanism, (3) endothermally decomposing inorganic salts which give rise to non-flammable gas such as H₂O, CO₂, NH₃ etc. e.g. Al(OH)₃, ammonium salts, CaCO₃ etc., (4) compounds that form glassy coatings, e.g. inorganic salts that melt and give coating preventing entry of O₂ and heat to the reacting phase, (5) molecules which reduce the volatility of flame resistant compound, (6) resin formers which act as coupling agents between the substrate and flame retardants, (7) compounds that act synergistically e.g. antimony compounds in the presence of halogens. The phosphorus-halogen and phosphorus-nitrogen compounds are also thought to act synergistically. The pertinent aspects of a few fire-retardant systems are discussed below.

1.10.1 Phosphorus compounds

Organic phosphorus compounds are successfully employed in fire retardation of a number of polymers [7,26,27,67]. Cellulosics [89] and polyurethanes [7,26,27,90] are two examples worthy of mention.
In polyurethanes also, the action of phosphorus based fire retardants appear to involve char formation [91]. FRs are expected to condense with the depolymerised isocyanates or amines forming thermally stable resins and char.

The char formation on a smoldering combustion is further enhanced and smoldering prevented with the additions of FRs.

Phosphorus compounds can also act thermally to break down the polymer for enhanced drip [92]. It is also reported that certain phosphorus compounds such as trimethyl phosphate, triphenyl phosphine oxide etc. act to modify the vapour phase processes [93,94].

In poly(ethylene terephthalate) and poly(methyl methacrylate), phosphorus FRs produce aromatic residue and char and the char is thought to act as a thermal barrier [95]. In general, phosphorus flame retardants act as an acid precursor in the solid phase to induce selective decomposition pathways that result in the reduction in the rate of fuel formation and an increase in charring [96].

1.10.2 Halogens

Halogen fire retardants function generally in the vapour phase by radical transfer mechanisms [67,97]. This is predominantly the mechanism of bromine containing fire retardants (1.4.2) The predominant flame retardant action of chlorine compounds is
centered in condensed phase process and is expected to increase char formation. Hilado and Casey reported that chlorinated rubber has a greater tendency to char than do styrene butadiene rubber, nitrile rubber etc. [98]. Bromine compounds are greatly twice as effective as chlorine compounds [67]. It is desirable for the fire retardant to decompose at lower temperature 60°C less than the decomposition temperature of the polymer [99]. Bromine compounds with decomposition temperature in the range 200-300°C go well with the decomposition of most of the plastics [67]. Another mechanism of halogen action postulates that the halogen alter the physical properties density and heat capacity of the oxidant mixture so that the flame propagation is effectively prevented [100]. Both dripping and char formation interfere with the energy feedback cycle.

1.11 FLAMMABILITY Vs THERMAL STABILITY OF POLYMERS

Flammability of a polymer decreases as its thermal stability increases. Thus thermally stable polymer structures that are inherently flame resistant can be built up. Fig. 1.3 gives structures of a few polymers that are inherently flame resistant. Their high cost and processing difficulties, however restrict their use to high performance applications. It becomes therefore apparent that use of flame retardants as additives or reactive systems is the only way open to make polymers that are flammable flame resistant. However, knowledge on thermal stability of polymers is required for the selection and use of appropriate flame retardants.
Fig. 1.3: Inherently flame resistant structures
1.11.1 Thermally stable polymers

Extensive investigations have been carried out in the field of thermally stable or high temperature resistant polymers for the last three decades. Research in this field has received impetus mostly from defence and space requirements owing to the need for ablative systems, high temperature adhesives and coatings and heat and flame resistant fibres. Among the three broad group of polymers, organic, organo-inorganic and inorganic, organic polymers find more extensive commercial importance as heat resistant polymers. For a polymer to be considered as thermally stable, the thermal stress in terms of time and temperature that the material has to withstand is to be defined. An increase in either of these factors shortens the expected life time, and if both are increased the use time is shortened logarithmically. H.H. Levine[101] has specified the total thermal stress for a heat resistant polymer to withstand as $177^\circ C (350^\circ F)$ for 30,000 hours, $260^\circ C (500^\circ F)$ for 1000 hrs, $538^\circ C (1000^\circ F)$ for 1 hour or $816^\circ C (1500^\circ F)$ for 5 minutes.

The most widely used method for comparing the thermal stabilities of high temperature polymers is dynamic thermogravimetric analysis (TGA). TGA data provides information about the threshold temperature at which major fragmentation occurs and is therefore an indication of the inherent stability of the polymer structure [102]. In TGA, the sample weight loss is continuously monitored at a given heating rate and in a specified environment
of vacuum, air or inert atmosphere. This method of analysis has the advantage of being rapid and reproducible when experimental conditions are carefully controlled. Since the heating rate employed in the analysis are relatively rapid (2-30°C/min), TGA curves are generally considered as an index of short term stability. One disadvantage is that TGA curves are sensitive to experimental variables such as particle size and heating rate. Because of the sensitivity of TGA to experimental conditions a strict comparison of thermal stabilities can only be achieved by analysing samples of interest under identical conditions.

At times, isothermal thermogravimetric analysis (IGA) is also used, though it is not as popular as TGA. In isothermal thermogravimetric analysis weight loss as a function of time is recorded at a specified temperature. One limitation of this method is that at high temperatures, appreciable weight loss is incurred during the heat up period before thermal equilibrium is reached. Both TGA and IGA are based on weight loss and provide no information on such processes as glass transition temperature (Tg) or crystalline melting point (Tm) which do not involve weight loss. These properties can be measured by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Both DTA and DSC are used for detecting endothermic or exothermic changes suffered by the polymer while heating the material at a constant rate. There are inherent limitations to these methods also due to variables such as heating rate,
sample size and others. Other methods of thermal analysis such as torsional braid analysis (TBA), thermomechanical analysis (TMA) and mass thermal analysis (MTA) have been applied only to very few high temperature polymers.

1.11.2 Structural and theoretical requirements for thermal stability

The greatest source of thermal stability of a polymeric material is the primary bond energy that exists between the atoms in the chain. The strength of a chemical bond imposes an upper limit on the vibrational energy that a molecule may possess without bond rupture. Since heat increases the vibrational energy, the heat stability is related to the dissociation energy of the bond. Bond dissociation energy between two atoms can be determined by measuring the energy of dissociation into atoms or the heat of formation from the elements. The bond energies between atoms capable of forming the polymer chains are given in Table 1.4 [104].

Besides the primary bond energies, polymers may also derive additional stability from secondary valence forces. These forces have a pronounced effect on Tg and Tm. Secondary valence forces may arise as a result of several effects. The two important are dipole-dipole interaction (upto 8.7 Kcal/mol) and hydrogen bonding (6-10 Kcal/mol).

The resonance stabilization of aromatic and heterocyclic
Table 1.4: Bond energies between the atoms capable of forming polymer main chain

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy, kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;al&lt;/sub&gt; - C&lt;sub&gt;ar&lt;/sub&gt;</td>
<td>98.0</td>
</tr>
<tr>
<td>C&lt;sub&gt;al&lt;/sub&gt; - C&lt;sub&gt;al&lt;/sub&gt;</td>
<td>83.0</td>
</tr>
<tr>
<td>S-S</td>
<td>63.0</td>
</tr>
<tr>
<td>Si-Si</td>
<td>53.0</td>
</tr>
<tr>
<td>P-P</td>
<td>53.0</td>
</tr>
<tr>
<td>B&lt;sub&gt;ar&lt;/sub&gt; - N&lt;sub&gt;ar&lt;/sub&gt;</td>
<td>115.0</td>
</tr>
<tr>
<td>C&lt;sub&gt;ar&lt;/sub&gt; - N&lt;sub&gt;ar&lt;/sub&gt;</td>
<td>110.0</td>
</tr>
<tr>
<td>C&lt;sub&gt;ar&lt;/sub&gt; - O&lt;sub&gt;ar&lt;/sub&gt;</td>
<td>107.0</td>
</tr>
<tr>
<td>Si-O</td>
<td>106.0</td>
</tr>
<tr>
<td>B-N</td>
<td>105.0</td>
</tr>
<tr>
<td>C&lt;sub&gt;al&lt;/sub&gt; - O&lt;sub&gt;al&lt;/sub&gt;</td>
<td>93.0</td>
</tr>
<tr>
<td>C&lt;sub&gt;al&lt;/sub&gt; - N&lt;sub&gt;al&lt;/sub&gt;</td>
<td>82.0</td>
</tr>
</tbody>
</table>
structures contribute substantially to the bond strength and thermal stability. The resonance energies of these cyclic structures range from 40-60 Kcal/mol.

Another very important requirement for heat-resistant polymers is high melting or softening temperature. High softening systems could be achieved by (1) crystallisation, (2) crosslinking and (3) chain stiffening.

Most of the thermally stable polymers are (1) polymers containing aromatic or heterocyclic units in the main chain, (2) fluorine containing polymers, and (3) inorganic and hetero-organic polymers such as silicones and boron containing polymers.

1.12 SELECTION OF FLAME RETARDANT ELEMENTS AND FLAME RETARDANT POLYMER SYSTEMS FOR THE PRESENT STUDY

A number of elements are known to give rise to flame retardancy to polymers. These are phosphorus, halogens, nitrogen, boron, arsenic, antimony, certain heavy metals etc. Phosphorus is well known to impart flame retardancy to oxygenated polymers such as cellulose, phenolics, polyurethanes etc. In order to enhance the FR effect, halogens such as Cl or Br is also incorporated into the FR. Although addition of Br to phosphorus containing polymers enhances the LOI values, the mechanism of the combined effect of P and Br is still to be settled. There are contradictory reports on the combined effects of phosphorus and bromine on the flammability of these polymers. It was shown in a recent work at RRL, Trivandrum, that CNSL based thermoset
polymers containing P and Br built into its structure exhibited good self-extinguishing property and ablation. The need for evaluating the thermal and flammability behaviour of model compounds containing phosphorus and bromine is thus apparent.

Phenolics and the analogous substituted phenolic polymers, for example, cardanolics (cardanol-formaldehyde resins and related resins are hereafter referred to as cardanolics) were selected for the present study because

1. Phenolics are highly oxygenated polymers where phosphorus is highly effective as FR
2. Phenol can easily chemically modified to introduce FR elements.
3. Cardanol has in its structure both hydrophobic and hydrophilic moieties that favours formation of wide spectrum flame retardants as discussed earlier.
4. Both phenol and cardanol are model compounds for incorporating P and Br so that their thermal and flammability behaviour could be correlated to have an understanding on the thermal and flammability behaviour of the ablative material mentioned earlier.
5. On going from phenol to cardanol the only structural difference is the aliphatic C\textsubscript{15} side chain. A study on the effect of the side chain on the thermal and
flammability behaviour could be interesting and is expected to lead to a complete understanding on these systems.

1.13 THERMAL DEGRADATION AND FLAMMABILITY OF PHENOLIC RESIN

1.13.1 Phenol-formaldehyde reaction mechanism

The conditions mainly pH and temperature under which reactions of phenols with formaldehyde are carried out, have a profound influence on the character of the products obtained [105]. Two prepolymer types are obtained depending on pH.

Novolaks are obtained by the reaction of phenol and formaldehyde in the acidic pH region. In general, the reaction is carried out at a molar ratio of 1 mol phenol to 0.75-0.85 mol of formaldehyde. Novolaks are mostly linear condensation products linked with methylene bridges of a relatively low molecular weight up to 2,000. These resins are soluble and permanently fusible, i.e. thermoplastic and are cured only by addition of a hardener, almost exclusively formaldehyde applied as HMTA to insoluble and infusible products.

Resols are obtained by alkaline reaction of phenols and aldehydes, whereby the aldehyde is used in excess. P/F molar ratios between 1:1 to 1:3 are customary in technical resols. These are mono- or polynuclear hydroxy methylphenols (HMP) which are stable at room temperature and by application of heat,
seldom of acids are transformed into three-dimensionally cross-linked, insoluble and infusible polymers (resits) over different intermediate stages (resitols).

1.13.2 The degradation of phenolic resins

The degradation, both thermal and thermo-oxidative of phenolic resins has been examined by Conley [106]. Infrared spectral analysis was used extensively in the investigations of phenolic-resin decompositions, as well as thermogravimetric analyses [107], elemental composition studies [107], gas chromatographic studies [108,109], model-compound and degraded polymer synthesis [110,111] and various curing procedures, to examine the effect of the degree of cure on the degradation of the phenolic-resin system [107-109,112]. The first step in the oxidation of phenolic resins can be visualized as shown in Fig. 1.4.

Fig. 1.4
Further oxidation resulted in evidence that was consistent with the following Fig. (1.5) which results in the formation of chain scission products.

Degradation above $250^\circ C$ and as high as $1000^\circ C$ has been examined [107-109, 113, 114]. Examination of the volatile products as a function of temperature and degree of pyrolysis showed that the chief products were CO, CO$_2$ and H$_2$O as expected for the extended oxidation of the resin. Paraformaldehyde, methane and aromatic products were also formed. From the available data,
it seems clear that oxidation is the primary mode of phenolic resin decomposition through approximately 700°C, regardless of whether the resin was decomposed in air, argon, or nitrogen atmospheres. The high-temperature pyrolysis (between 700 and 1000°C) of phenolic resins in vacuo was studied by mass spectral thermal analysis and the reactions which have been proposed to account for the observed product types are shown in Fig. 1.6 [109].

From the data reported concerning phenolic resin degradation it is possible to suggest that regardless of the particular resin species present before curing, the degradation processes occurring at elevated temperatures are dependent upon the thermal and oxidative stability of the dihydroxy diphenyl methane unit, and therefore these polymers all behave similarly from a chemical viewpoint once the curing processes are complete.

1.13.3 FLAME RETARDATION IN PHENOLIC RESINS

In general, phenolics are considered to have moderate nonflammability characteristics. They vary from slow burning to self-extinguishing. The rapid loss of volatiles below the ignition temperature leaves a carbonaceous residue which is quite stable [106]. Within a short time the char undergo a highly exothermic reaction which raises the internal temperature of the material. Such reaction characteristics strongly suggest the formation of peroxide species in high concentration by a carbon-radical scavenging process during the cooling stage. Decomposition of
Fig. 1.6: Proposed char forming reactions in phenolic resin system
the peroxidic species, is so highly exothermic that the char becomes incandescent.

However, most of the technology concerning flame retardation of phenolic resins involves either the incorporation of substances known to exhibit flame-retarding properties into the backbone structure of the organic polymers or the addition of various compounds or combinations of compounds into the resin system to impart flame-retardant characteristics [106].

1.13.4 Phosphorus and nitrogen compounds

Various types of phosphorus compounds have been added to phenolic resins to impart improved flame resistance [115]. Approximately 6% by weight of phosphorus in a phenolic resin will render it self-extinguishing. About 2% P and 2% N in a phenolic will also have the same effect [116]. These additives may facilitate the formation of ring structures which produce charring and aid flame retardancy.

1.13.5 Halogen compounds

Halogen compounds make phenolic resins more flame resistant but at the expense of increased smoke emission in some cases. Novolaks can be chlorinated by chlorine gas for improved flame retardancy [117]. Laminates, coatings, castings and molded articles were prepared from this composition and are self-extinguishing.
1.13.6 Miscellaneous

Boron compounds also improve the flame retardancy of phenolic compounds. It has been found that by adding aluminium chloride to an aqueous acid curing phenolic formaldehyde condensate its flame retardancy and self-extinguishing characteristics are greatly improved [118]. Nonfriable, self-extinguishing foamed constructions can be prepared by coating expanded phenolic panels with solutions of alkali-metals or alkaline-earth-metal silicates or fluoro silicates [119]. Table 1.5 lists some commercially available flame retardants for phenolics.

Table 1.5 : Commercial flame retardants for phenolics

<table>
<thead>
<tr>
<th>Organic additive</th>
<th>Trade name</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Phosphate esters</td>
<td>Escoflex CDP</td>
<td>East Coast Chemical</td>
</tr>
<tr>
<td></td>
<td>Antoxal</td>
<td>Eronel Industries</td>
</tr>
<tr>
<td>2. Cresyl diphenyl phosphate</td>
<td>Escoflex CDP</td>
<td>East Coast Chemical</td>
</tr>
<tr>
<td></td>
<td>Santicizer 140</td>
<td>Monsanto</td>
</tr>
<tr>
<td></td>
<td>Disflamoll DPK</td>
<td>Naftone</td>
</tr>
<tr>
<td></td>
<td>Phosflex 112</td>
<td>Stauffer Chemical</td>
</tr>
<tr>
<td>3. Halogenated organic polyphosphate</td>
<td>Phosgard C-22-R</td>
<td>Monsanto</td>
</tr>
<tr>
<td></td>
<td>PC-45</td>
<td>Upjohn</td>
</tr>
<tr>
<td>4. Chlorinated diphenyls and polyphenyls</td>
<td>Arroclor</td>
<td>Monsanto</td>
</tr>
<tr>
<td></td>
<td>Clphen</td>
<td>Naftone</td>
</tr>
<tr>
<td>Organic additive</td>
<td>Trade name</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>------------------</td>
<td>------------</td>
<td>--------------</td>
</tr>
<tr>
<td>5. Tris(2-chloroethyl) phosphate</td>
<td>TCEP, Fyrol CEF</td>
<td>British Celanese, Stauffer Chemical</td>
</tr>
<tr>
<td>6. Trichloropropyl phosphate</td>
<td>TCPP</td>
<td>British Celanese</td>
</tr>
<tr>
<td>7. Tris(2,3-dibromopropyl) phosphate</td>
<td>Firemaster T23P, LV-T23P, Fyrol 32 B and HR-32</td>
<td>Michigan Chemical, Great Lakes Chemical, Stauffer Chemical</td>
</tr>
<tr>
<td>8. Box dimer C&lt;sub&gt;10&lt;/sub&gt;C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>Dechlorane</td>
<td>Hooker Chemical</td>
</tr>
<tr>
<td>9. Chlorinated paraffin</td>
<td>Chlorowax liquids and solids, CP-40 and CU-50</td>
<td>Diamond Shamrock, Hooker Chemical</td>
</tr>
<tr>
<td>10. Chlorinated organic</td>
<td>Dechlorane plus 602</td>
<td>Hooker Chemical</td>
</tr>
<tr>
<td>11. Antimony trioxide dispersions</td>
<td>HSC-P series</td>
<td>Harwick Podel Industries</td>
</tr>
<tr>
<td>12. Barium metaborate dispersions</td>
<td>Busane 11-MI</td>
<td>Ware Chemical</td>
</tr>
<tr>
<td>14. Di-(polyoxyethylene)-hydroxy methyl phosphonate (reactive type of additive)</td>
<td>Fryol HMP</td>
<td>Stauffer Chemical</td>
</tr>
</tbody>
</table>
1.14 CARDANOL BASED POLYMERS AND THEIR FLAME RETARDANCY

Cardanol, obtained from the plant Anacardium occidentale L. has been shown to be a monohydric phenol with a \( C_{15} \) side chain in the meta position and is obtained from technical grade cashew nut shell liquid (CNSL) by vacuum distillation at 3-4 mm Hg and the fraction distilling at 228-235\(^{\circ}\)C was collected [120]. The physical properties of cardanol are given in Table 1.6.

Table 1.6: Physical properties of cardanol

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. (^{\circ})C</td>
<td>228-235(^{\circ})C (3-4 mm Hg)</td>
</tr>
<tr>
<td>Colour (Lovibond, Red)</td>
<td>Yellow (1.5-3.5)</td>
</tr>
<tr>
<td>Freshly distilled</td>
<td>Yellow (1.5-3.5)</td>
</tr>
<tr>
<td>Viscosity (30(^{\circ})C) cP</td>
<td>45-52</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.50 (\mu)</td>
</tr>
</tbody>
</table>

Cardanol is a mixture of four components differing in the degree of unsaturation of the side chain (Fig. 1.7) [121]. Molecular formula, molecular weight and percentage composition of each component of cardanol are given in Table 1.7. The percent composition however may vary depending upon the source, method of extraction etc. There have been many attempts to separate the components of cardanol and foremost among them is the work of Tyman [122-124].
Fig. 1.7: Structure of cardanol

Table 1.7 : Chemical composition of cardanol

<table>
<thead>
<tr>
<th>Component</th>
<th>M.wt.</th>
<th>%</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardanol with saturated side chain</td>
<td>304</td>
<td>5.4</td>
<td>C_{21}H_{36}O</td>
</tr>
<tr>
<td>Cardanol with one double bond in the side chain (monoene)</td>
<td>302</td>
<td>48.5</td>
<td>C_{21}H_{34}O</td>
</tr>
<tr>
<td>Cardanol with two double bonds in the side chain (diene)</td>
<td>300</td>
<td>16.8</td>
<td>C_{21}H_{32}O</td>
</tr>
<tr>
<td>Cardanol with three double bonds in the side chain (triene)</td>
<td>298</td>
<td>29.3</td>
<td>C_{21}H_{30}O</td>
</tr>
</tbody>
</table>
The structure of cardanol was established through the painstaking efforts of a series of workers such as Dawson and Wasserman [125], Paul and Yeddanappalli [126], Tyman and his group [127], Gedam et al etc. One of the significant aspects of its structure is its amenability to chemical modifications and polymerisations. An examination of Fig.1.7 shows that cardanol can undergo chemical modifications at the hydroxyl group, substitution reactions on the phenolic ring and oxidation/addition reactions at the side chain. The presence of active hydrogens of the phenolic ring and the unsaturation in the side chain make it polymerisable either by step reaction polymerisation or by chain reaction polymerisation or a combination of both as is practised in the preparation of resins for brakelining [128]. Cardanol thus possess interesting structural features for development of speciality polymers.

1.14.1 Chemical modification of polymerization of CNSL and cardanol.

The Regional Research Laboratory, Trivandrum, has recently developed two prepolymers ANORIN-38 and ANORIN-44 [129-132] by reaction with orthophosphoric acid followed by halogenation. The presence of highly acidic environment oligomerises the phosphorylated molecules into a prepolymer simultaneously. ANORIN-38 contains only P (8%) and ANORIN-44 contains both P and Br (25%).
Both ANORIN-38 and ANORIN-44 are highly reactive with aldehydes, amines etc. [130,131]. They can be converted to thermoset products [130-132]. The limiting oxygen index of some of these products are given in Table 1.8.

Table 1.8 : Limiting oxygen index values of a few fully cured Anorin series fire-retardants

<table>
<thead>
<tr>
<th>Resin</th>
<th>LOI value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phos. CNSL</td>
<td>38.0</td>
</tr>
<tr>
<td>Phos. and bromine containing resin</td>
<td>43.5</td>
</tr>
<tr>
<td>NR + ANORIN-38</td>
<td>21</td>
</tr>
<tr>
<td>NR + ANORIN-44</td>
<td>28</td>
</tr>
<tr>
<td>NR + ANORIN-44 + Sb_2O_3</td>
<td>42.0</td>
</tr>
</tbody>
</table>

ANORIN-38 showed excellent miscibility and compatibility with a wide range of polymers. It showed comparatively good FR activity with polyethylene and polyurethane. Both ANORIN-38 and ANORIN-44 increased the mechanical properties of natural rubber [133] and enhanced processability. Another interesting observation was that ANORIN-44 in combination with Sb_2O_3 showed excellent synergism with natural rubber.

The use of halogen definitely gives rise to smoke, but blending with appropriate amounts of boric acid or aluminium
trihydrate reduced the smoke level completely without deleteriously affecting the properties. The present data obtained with these two prepolymer indicators a wide range of applicability without deleterious effects and above all cost effectiveness, a factor that controls the market conditions. A composite panel prepared from fully cured ANORIN-44 does not burn even under oxy-acetylene flame around at 30°C. This material was found to show excellent ablation characteristics.

1.14.2 High performance polymers from cardanol

The structural difference between phenol and cardanol is only the C15 unsaturated side chain and hence cardanol undergoes most of the reactions of phenol. Thus cardanol can be polymerised with formaldehyde to give resols and novolaks [134]. The presence of the side chain gives it an added advantage that it can be polymerised by chain reaction methods as well. This gives rise to opportunities for selection and control on polymerisation techniques for a particular product. For example, the preparation of resins for brakelining is reportedly made by making use of an acid catalysed side chain polymerisation followed by the conventional formaldehyde condensation. Apart from the variety in polymerisation reactions cardanol can also undergo chemical modifications at the hydroxyl, ring and the side chain. Moreover, the hydrocarbon side chain itself by its very presence imparts new properties such as internal plasticization, flexibility etc. [121]. A study by Pillai et al [135]
have shown that high performance and speciality polymers could be produced from cardanol by a variety of methods such as:

1. Prepolymer route:

   1. Functionalisation at the hydroxyl group

   \[ \text{OH} \quad \overset{\text{R}}{\text{R}} \]

   2. and oligomerisation

   can be used in variety of ways such as ion exchange resins and polymeric fire-retardants, depending on the functional group can be further polymerised and processed into thermoset plastic products having higher impact properties than do phenolics

2. Dimer route:

   \[ \text{OH} \quad \overset{\text{R}}{\text{R}} \]

   Dimerisation

   \[ \text{OH} \quad \overset{\text{R}}{\text{R}} \]

   dimer

   Copolymerisation with rigid and bifunctional monomers

   Linear chain polymers with repeating sequences of hard and soft segments. Possibility of formation of liquid crystal polymers and thermoplastic elastomers

3. Oxidation route:

   \[ \text{OH} \quad \overset{\text{R}}{\text{R}} \]

   Chemical modification at the hydroxyl group and oxidation

   \[ \text{OR}_1 \quad \overset{\text{R}}{\text{R}}'\text{COOH} \]

   Copolymerisation with rigid rod monomers

   Liquid crystal polymer
When studies were initiated to develop speciality polymers from cardanol, it became apparent that there exists a wide gap between the technology and scientific understanding. There has been a total lack of data on kinetics and mechanism of polymerisation of cardanol except the work of Misra and Pandey who reported the kinetics of alkaline catalysed formaldehyde condensation [136]. It is well known that it is not possible to apply modern methods of polymer science and technology for the development of speciality polymers without basic data on polymerisation characteristics and structure-property correlations. So kinetics and mechanism of polymerisation of cardanol were studied using acid catalysts such as $\text{H}_2\text{SO}_4$, $\text{H}_3\text{PO}_4$ and Lewis acids such as $\text{BF}_3$ etherate [137]. These studies showed that cardanol undergoes oligomerisation under acidic conditions through the side chain unsaturation and the oligomerisation is initiated by protonation of the side chain followed by cationic chain growth. These studies led to the development of the prepolymer technology where cardanol was functionalised at the hydroxyl group using orthophosphoric acid [135]. The high acidic conditions simultaneously initiate oligomerisation giving rise to a prepolymer as the phosphorylated product. It was found that formation of the prepolymer (PCP) is advantageous in the sense that it can be used as a multi-purpose resin because of the possibilities of its different end products as shown earlier. The introduction of the phosphate group raised the LOI value from 21.0 to 35.0 for the amine cured product and the lap shear strength for wood to wood bonding increased 500 fold (Table 1.9).
Table 1.9: LOI value of cured PCP/PCNSL resin

<table>
<thead>
<tr>
<th>Resin</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCP (HMTA) cured</td>
<td>35.0</td>
</tr>
<tr>
<td>PCP (Paraformaldehyde) cured</td>
<td>33.0</td>
</tr>
<tr>
<td>Brominated PCP</td>
<td>42.0</td>
</tr>
<tr>
<td>Cardanol-formaldehyde (Novolak)</td>
<td>21.0</td>
</tr>
<tr>
<td>CNSL-formaldehyde</td>
<td>21.0</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>16.9</td>
</tr>
<tr>
<td>PCP-Polyethylene</td>
<td>24.5</td>
</tr>
</tbody>
</table>

When it was used as matrix resin for asbestos fibre based brakelinings, a fade value as low as 19% was registered.

The presence of both hydrophilic and hydrophobic groups in the same molecule makes PCP an ideal candidate for wide spectrum [138] polymeric flame retardant. PCP resins were found to be compatible with a wide spectrum of polymers such as polyolefins, polyurethane and natural rubber.

One of the significant observations has been that introduction of bromine into the phosphorylated prepolymer imparts the property of ablation to the polymer [132]. When tested by oxy-acetylene panel experiments conducted as per ASTM method, the PCNSL based ablative reinforced thermoset product gave a
total burn through time of 97 sec compared to 88 sec for conven­tional phenolic and 200 sec for a blend of PCNSL with phenolic resin suggesting synergism. Thermal analysis of brominated PCP did not show any significant contribution to ablation from thermal stability and char yield. So it was inferred that the ablation process might arise from the endothermic liberation of vapours of hydrobromic acid followed by transpiration cooling effected through the decomposition gases of the side chain [139].

In another study, it was shown that cardanol-formaldehyde (CF resins, both resol and novolak) form semi-interpenetrating networks with PMMA [140]. Although interpenetration of PMMA increases the mechanical properties only marginally, it showed a stabilization in PMMA at $350^\circ$C from 50% decomposition to 15%. However, the Tg of CF registered an unusual increase from $128^\circ$C to $144^\circ$C suggesting restriction in the segmental motion of the CF phase brought about by mixing with another rigid polymer such as PMMA [141].

One of the remarkable achievements in converting cardanol into high temperature resistant polymer was the successful prepara­tion of a homopolyester and a thermotropic liquid crystalline polymer [142]. When cardanol was subjected to phase transfer catalysed $\text{KMnO}_4$ oxidation the side chain was cleaved and oxidised to 3-HPOA (8-(3-hydroxy phenyl) octanoic acid). 3-HPOA is a bifunctional monomer possessing both 'kink' structure and flexible segment ($-(\text{CH}_2)_7$) built into the same molecule.
These structural features are useful in bringing down the transition temperature of intractable liquid crystalline polymers such as P-HBA so that they could be made processable. While HPOA was copolymerised with P-HBA, the LC copolymers showed a transition at $256^\circ C$ which is much lower than those of the commercial products Vectra and Xyder. The isotropic melting of the polymer occurred at $409^\circ C$.

It appears that the opportunities for chemical transformation of cardanol into high value polymers are vast.

1.15 SOME PROSPECTIVE APPROACHES TO MORE EFFICIENT FLAME RETARDANT SYSTEMS [143]

1.15.1 Vapour phase flame retardants

The widely used flame retardant systems which contribute hydrogen chloride or hydrogen bromide to the vapour phase may be acting by not much more than a physical heat capacity effect [144]. The work on tris (dichloroisopropyl phosphate) in polyurethane foams by Weil et al also suggests a physical mode of action [145]. Flame studies in hydrogen oxygen flames show vaporized metals active as hydrogen atom recombination catalysts. Therefore it can be said that vapour phase flame retardants may be found for use in plastics.

Efficient physical barriers to heat, air and pyrolysis products

Carbonaceous char barriers may be formed by the normal
mode of polymer burning and besides the reduction in the amount of material burned, the char may act as a fire barrier. For polymers with low char forming tendencies, such as poly olefins, one approach to get a char is to add a char-forming additive (generally bearing a resemblance to intumescent coating compositions) [146].

1.15.2 Permeability of carbonaceous foam

To work optimally the char or similar barrier should be coherent, adherent, oxidation-resistant and low in permeability to heat and gases. A closed cell foam prevents the penetration of combustion vapors and air through char layer. Gibov et al [147] showed that the incorporation of boric acid and ammonium phosphates helped cut down penetration of the char. The cracking or defoliation of the char can also cause exposure of the underlying material to burning. A general way to improve the coherence of char may be to use formulations of improved intumescent coatings [148], (by use of high aspect ratio inorganic filler).

1.15.3 Oxidative destruction of the char layer and its prevention

The char layer from a burning polymer while it exerts protective action, is itself vulnerable to oxidation. Studies on preventing combustion of carbon fibers, incorporation of borates, phosphates, or low melting glasses has been shown to be effective [149,150]. Other types of barriers include, (1) glassy coatings
using low melting glasses, (2) glassy foams, (3) carbonaceous foams with substantial carbon content, (4) fluorocarbon films and coatings, and (5) metallic surface coatings. The char enhancing action of magnesium soaps, siloxane block polymers [151] and the char stabilizing action of lead salts [152] were studied in polyolefins by general electric investigators.

1.15.4 Free radical inhibitors in the condensed phase

Surface (condensed phase) oxidation plays a major part in the flaming degradation of polyolefins [153]. An antioxidant system in the condensed phase should have a flame retardant effect.

1.15.5 Catalytic modes of flame retardant systems

Certain catalytic modes have been well exploited in flame retardant systems, namely the dehydrating action of compounds which yield strong acids under flaming or smoldering conditions. If a hydrocarbon could be made to undergo oxidative dehydrogenation to form water and char, its heat of combustion could be cut to about one-third the heat of complete combustion to CO₂ and H₂O and this would afford a drastic reduction in flammability. There are some reports of the dehydrogenation/oxidative dehydrogenation mode of catalysis for flame retardation.
1.15.6 Polyblends of flame retardant with non-flame-retardant plastics

Since the chemical modification of polymers for improved flame retardancy increases cost and deleteriously affect some other properties, from a commercial standpoint, the present trend is to utilize polyblending. For example, in the case of PPO-PS blends, the good char forming ability of the PPO greatly helps flame retardancy [154].

1.15.7 Synergism

The quantitatively-measured flammability of a polymer containing differing levels of a flame retardant is usually not linear, but is more likely to be synergistic or antagonistic. Careful attention to quantitative activity vs concentration relationships, to the effect of interaction terms in combinations and careful observation of the manner in which one mode of action supports and reinforces another seems to lead to highly efficient flame retardant systems.

1.16 FLAME RETARDATION BY INSITU GENERATION OF THERMALLY STABLE STRUCTURES

The existence of innumerable polymers whose mechanisms of combustion vary, calls for various approaches for flame retardation. As has already seen from the earlier discussions, it is clear that inhibition of flammability could be achieved by modifying reactions in the condensed phase or vapour phase processes of a burning polymer. It has already been shown that a
a number of fire retardants function by increasing the char yield. Research should be directed to find a catalyst or a comonomer that catalyses the reaction of the polymer to yield ultimately carbon and water. Thus, it is possible to use a more stable aliphatic bromine compound that gives less smoke. In a recent study on brominated phenols containing allyl side chain, the allyl group is said to impart higher stability to the polymer. Similarly alicyclic structure that give more permanency and greater stability could be thought of. Coupled with such fire-retardants a greater understanding on the control of pyrolysis and control of dripping of polymers are needed.

It has been shown that though comparatively less flammable the weak portions of the phenolics are the methylene bridges. The methylene bridges could be replaced by more thermally stable curing agents such as 4-hydroxy benzoic acid, diphenols, furfural etc.

Fenimore and Martin in their study on oxygen index of polymers found that the LOI can be related to the char forming ability of the polymer. This possibility indicates that polymer flammability possibly depends more on the condensed phase reactions.

Piechota found definite correlations between raw materials formulation and fire-retardancy of polyurethane foams. Quin studied the effect of structural unsaturation and found that LOI
increased with the unconjugated unsaturation and simultaneously the char forming tendency also increased.

The presence of certain structure or segments in a polymer is found to enhance thermal stability. Thus inducing the formation of polycarbodiimide structure and trimerization of isocyanates into thermally stable isocyanurates are two examples that could be applied in the polyurethane system.

\[
2 \text{R N CO} \rightarrow \text{NR = C = NR}
\]

\[
3 \text{R N CO} \rightarrow \text{Isocyanurate}
\]

Since these structures contribute to stiffness, it would be difficult to build units of high thermal stability and still maintain flexibility.

Anderson has shown that weight loss in polyurethane foam decreases with an increase in cross-link density. Aromatisation, cyclisation and cross-linking of polymer during pyrolysis may favour enhanced char formation.

Certain organic acids such as pyromellitic acid, trimellitic acid and maleic acid are good char formers and oxalic acid
and trimellitic acids are combustion modifiers. Ascorbic acid is a good char stabiliser. So polyurethane foam could be made fire retardant without smoke generation by using a combination of char former, combustion modifiers and char stabilizers.

It has been shown that the decomposition reactions of polyurethane can be altered by the addition of aromatic alcohols and aldehydes such as benzyl alcohol, benzaldehyde etc. These additives are believed to function by condensing with the depolymerised acids to form thermally stable resins and char.

When the overall function of a flame retardant including inhibition of smoke and toxic gas is considered, the data shown in this section are significant in the sense that they direct towards a higher level of safe flame retardation through appropriate understanding and control of structures and mechanisms. Possibly, this could turn out to be a better way of looking at the problems rather than going unscrupulously synthesising unlimited number of chemicals for flame retardation. However this attitude should go along with improved methods for measuring flame retardant effectiveness.

1.17 WIDE SPECTRUM FLAME RETARDANTS

This concept has been discussed earlier. This approach may be adopted to develop more effective flame retardants.
SCOPE AND OBJECTIVE

The significance and the need for flame retardation of polymeric materials have been brought out in the preceding sections. It is clear from this treatment that although there are innumerable flame retardants with excellent LOI values there is no FR till today that meets all the requirements that specifies an intended use. A review of various approaches to the use of FR has shown that there are definite advantages in using FR, (a) built into the structure of the polymer, and (b) as a pre-polymer. The admirable qualities of wide spectrum flame retardants and their advantages have also been discussed. When all these aspects were considered, it was thought fit to select the system based on phenol (because of its amenability to chemical modifications so that the desired FR element could easily be introduced) and substituted phenols (for example, cardanol from which wide spectrum FR could be developed). So the objectives of the present work are the following:

1. In developing wide spectrum FR based on cardanol, it was evident that there are not enough data on the polymerisation characteristics of cardanol. So it was thought necessary to study kinetics and mechanism of polymerisation of cardanol using BF$_3$ etherate as initiator.

2. To synthesise and characterise wide spectrum FR pre-polymers and polymers from cardanol containing FR elements
such as P and Br and to evaluate their thermal and flammability behaviour (the elements P and Br were selected because an earlier work at the R.R.L., Trivandrum has shown that CNSL based thermosets containing P and Br exhibit ablation phenomenon).

3. To study separately and together the effect of P and Br on the mechanism of flame retardation with a view to assessing their suspected synergism-additive behaviour.

4. Phenolic resins are believed to degrade by a thermo-oxidative process. Introduction of phosphorus is expected to enhance resistance to thermo-oxidation. Direct phosphorylation of phenolics gives rise to early gelation and so in the present work P is introduced at the monomer level. So the fourth objective is to synthesise and characterise P and Br containing phenolics and evaluate their thermal and flammability behaviour.

5. Polyphosphate esters of phenol are well studied and are known to give good thermal and flammability behaviour. Replacing phenol with cardanol is expected to impart additional property such as improved processability, wide spectrum FR effects etc. So the fifth objective is to synthesise and characterise polyphosphate esters based on cardanol with hydroquinone, bisphenol, tetrabromobisphenol and phenolphthalein and to evaluate their thermal and flammability behaviour.
6. To study the effects of these FR on another polymer and to evaluate the relative performance of monomeric FR vis-à-vis polymeric/wide spectrum FRs, it is proposed to prepare blends of a few of these FRs with polyethylene and study their thermal and flammability behaviour.

7. As the element boron is known to give good thermal and flame-retardant characteristics, it is proposed to synthesise and characterise boron containing polymers of cardanol and phenol and evaluate their thermal and flammability behaviour.
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