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## Introductory Chapter: Flame Retardants

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Additional information is available at the end of the chapter

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### 1. Introduction

Fire is one of the greatest inventions of human beings, no doubt. However, if not managed cautiously, it may be deadly hazardous causing inestimable harm to life and property. Polymeric materials comprising of hydrocarbon chains are prone to burning when exposed to fire, releasing enormous heat, flame and smoke. With polymers all around us today, the great significance of fire/flame retardant materials [FiRs] in our lives can be judiciously realized. Polymers can be made fire/flame retardant [FiR] by the inclusion of micro- and nano- FiR fillers or by the incorporation of FiR compounds in their backbone. This review paper focuses on the basic aspects of FiR polymers such as their composition, types of fillers and additives used, and their applications. The review also discusses briefly about bio-based FiRs, while emphasis will be particularly made on the developments in the field of vegetable oil-based FiRs and their applications.

Polymers celebrate prominent place in our daily lives. The extensive uses of polymers also raise our concerns and requirements for fire safety, as the polymers are highly combustible, being mainly made up of carbon and hydrogen. When exposed to fire, polymers burn rapidly, releasing lot of heat and smoke, causing great damage to life and property. Thus, the use of FiRs has become mandatory from viewpoint of safety of life and environment. FiRs stop or inhibit the polymer combustion process, acting physically or chemically, by interfering with heating, pyrolysis, ignition, thermal degradation, i.e., various processes involved in polymer combustion. Thus, to improve FiR properties of polymers, it is very important to understand combustion which requires three main candidates: heat, oxygen and fuel (combusting material). When a substance is heated, its temperature rises to its pyrolysis temperature, and it produces char, liquid condensates and some gases (flammable and non-flammable). At still higher temperature, combustion temperature, these flammable gases produce large amount of light, heat and smoke on combining with oxygen (**Figure 1**).

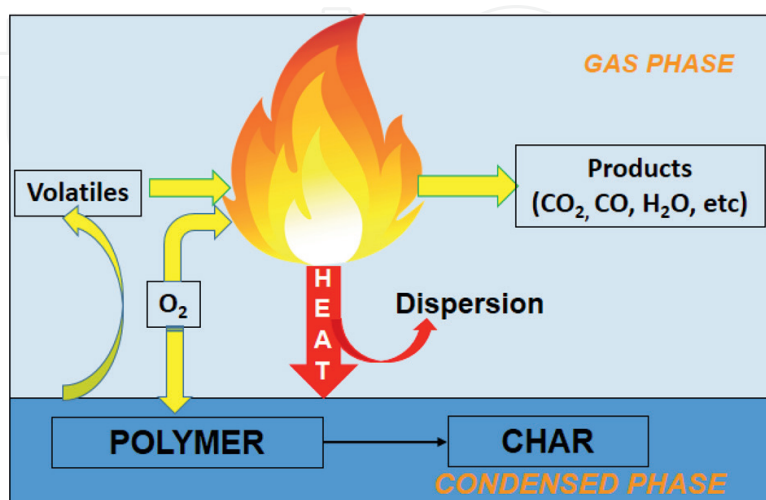
The combustion cycle thus continues with the help of heat produced by combustion [1]. The disruption in this combustion cycle can cause flame retardancy, and can be achieved by the following mechanisms (**Figure 2**):

- incorporation of such materials in polymers that, on exposure to heat do not allow the temperature of material to rise to pyrolysis temperature,
- incorporation of materials that produce more non-flammable by-products and char during pyrolysis; the latter acts as an obstacle to heat and mass transfer between gas and condensed phase (condensed phase mechanism), and
- using FiRs that cause reduction in  $O_2$  concentration in flame zone, by releasing non-flammable gases (gas phase mechanism).

FiRs comprise of additive FiRs, compounds (mineral fillers, hybrids) that are incorporated in polymers but they react with polymers only at higher temperatures, that is at the onset of fire, and reactive FiRs that are incorporated in polymer chains during synthesis.

There are many types of FiRs based on:

- minerals (oxides and hydroxides of metals, ex: magnesium hydroxide, aluminum hydroxide, calcium carbonate; borates, ex: zinc borates)
- halogens
- phosphorus
- silicon
- nitrogen
- nanoparticles



**Figure 1.** Combustion cycle.

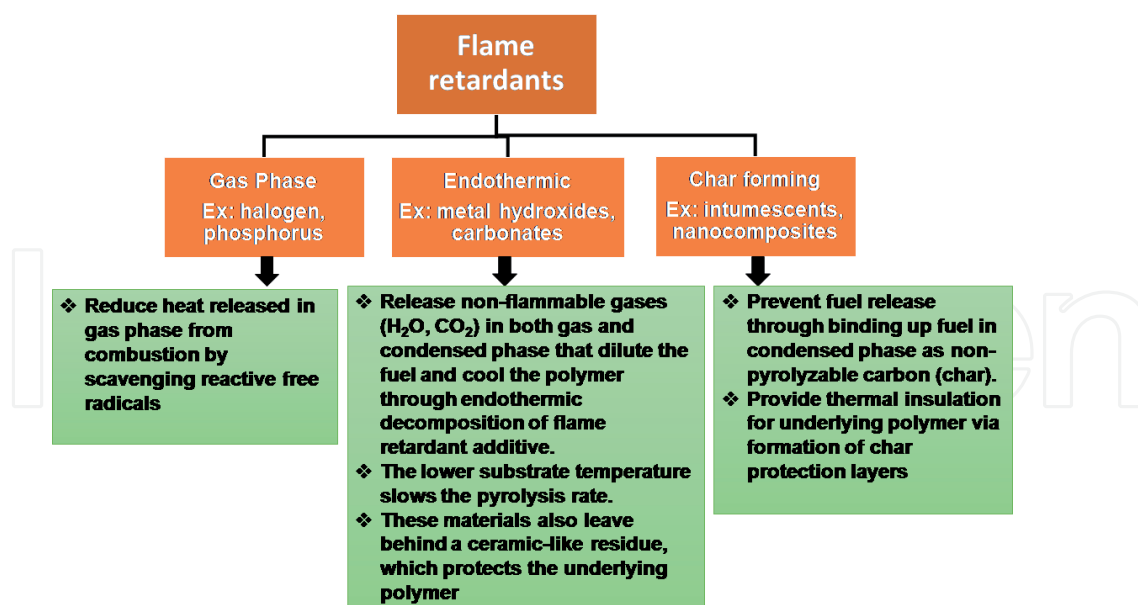


Figure 2. Types of FiRs and their mode of action.

Some examples of FiRs containing bromine and phosphorus are given in Figures 3 and 4.

Nanoparticles not only improve mechanical strength but also enhance flame retardance of polymers. These include nanoclays, carbon nanotubes, sepiolites, silsesquioxane, silica and titanium nanoparticles, nano metal oxides and others (Figure 5). Figure 6 provides mechanism of flame retardance by nanoclays in a polymer composite. The selection of a particular nanoparticle as FiR, in polymer composite systems, depends upon its chemical structure and geometry.

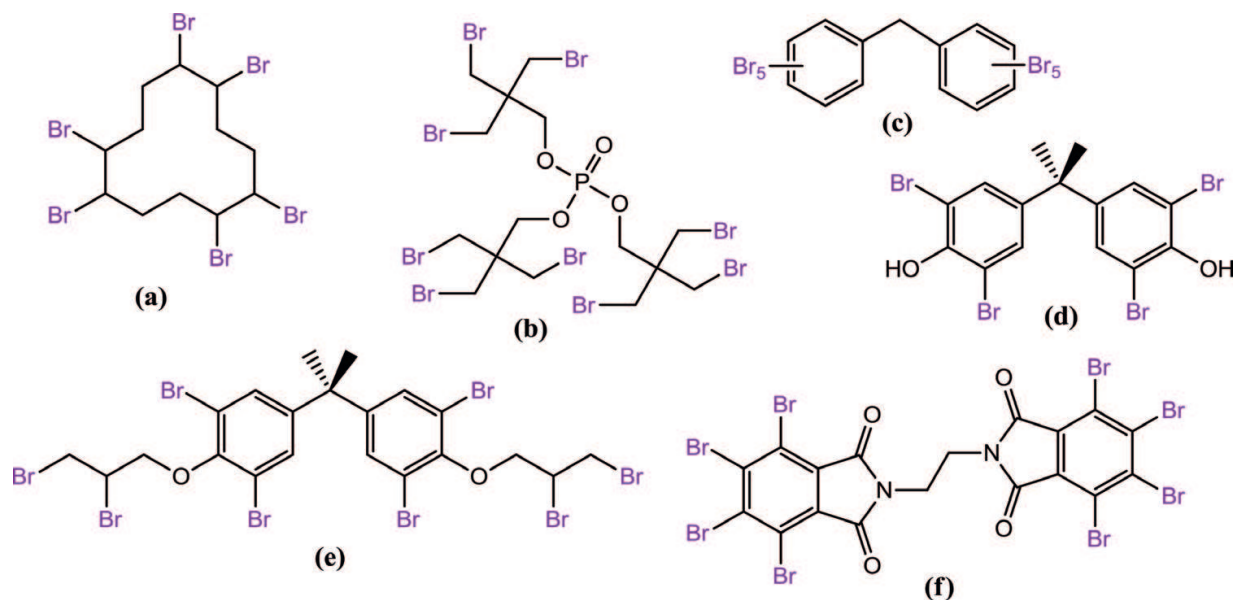
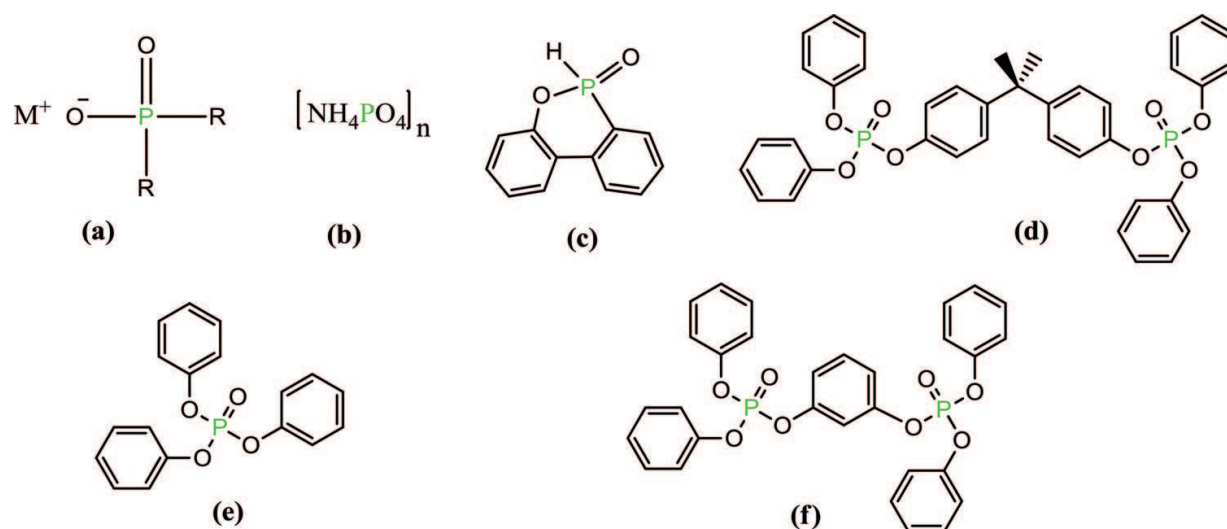
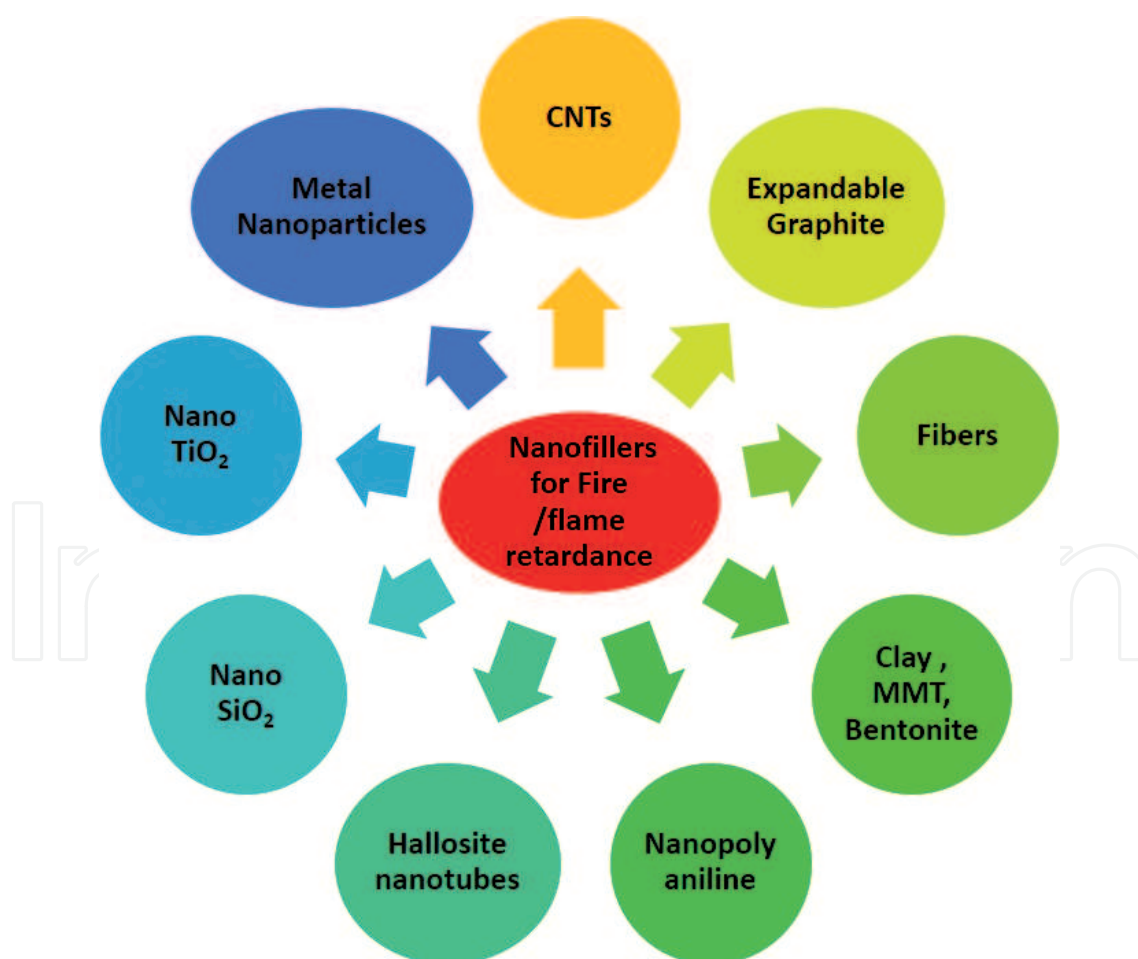


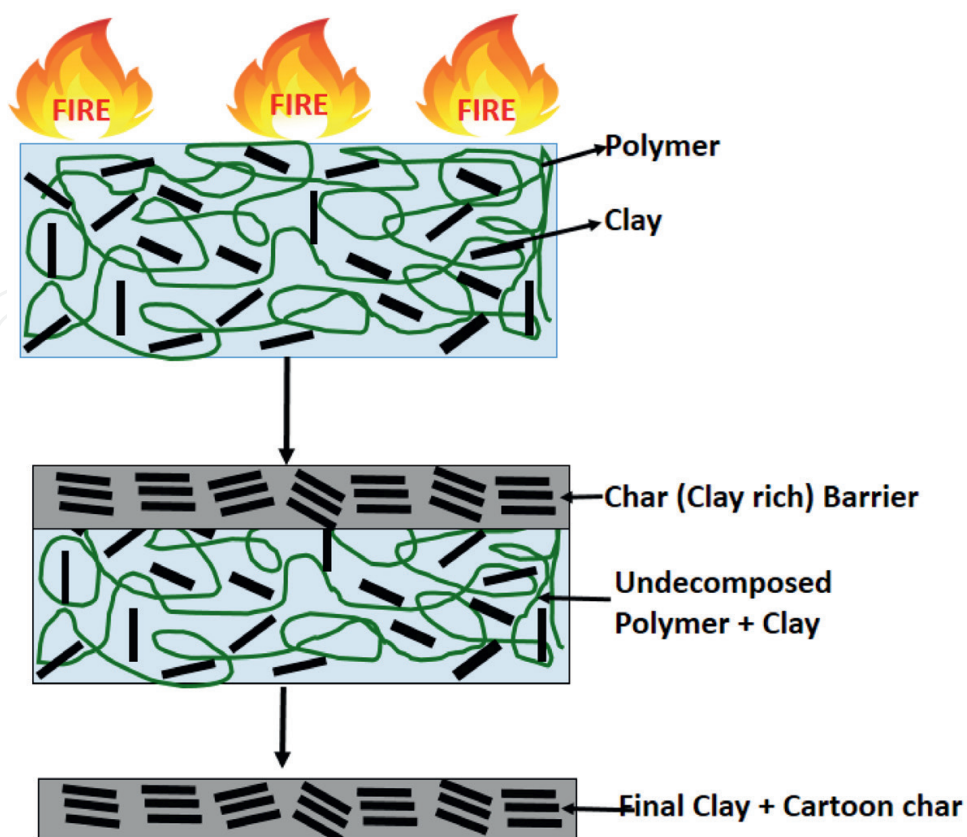
Figure 3. Bromine-based aliphatic and aromatic FiRs (a) hexabromocyclododecane, (b) tris (tribromoneopentyl) phosphate, (c) decabromodiphenyl ether, (d) tetrabromo bisphenol A, (e) bis (2,3-dibromopropylether) tetrabromo bisphenol A and (f) 1,2-ethylene bis (tetrabromophthalimide).



**Figure 4.** Phosphorus containing FiRs (a) phosphinate salts ( $M = Al, Zn$ ,  $R = alkyl$ ), (b) ammonium polyphosphate, (c) 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, (d) bisphenol A diphosphate, (e) triphenylphosphate and (f) resorcinol diphosphate.



**Figure 5.** Some nanofillers used for fire/flame retardance.



**Figure 6.** Mechanism of flame retardance by nanoclays.

FiRs are tested by UL 94 V, limited oxygen index, cone calorimeter, and other tests. Several prospects of FiRs have been described in detail in previously published reviews [1–3].

The strategies to improve fire/flame resistance are primarily governed by the nature and chemical structure of polymers, their mode of decomposition, fire safety level required and the performance of the polymer product. Today, our rising concerns towards human health and environment protection, together with the fire safety of life and property, have driven us to develop FiRs that are cost effective, less/non-toxic, environment-friendly and are conducive to optimum fire safety performance. Bio-based FiRs are ideal alternatives in this context, discussed briefly in following section.

## 2. Bio-based FiRs

Fast depleting petroleum resources, high prices of petro-based chemicals, health and environmental hazards caused by these, worldwide legislations and also ban on the use of some compounds have drastically influenced the world of polymer materials, so also FiRs. Thus it has become imperative to use bio-based resources in the field of FiRs. Biomolecules such as carbohydrates (cellulose, starch, chitosan, alginates), proteins, lipids (vegetable oils, cardanol) and phenolic compounds (lignin, tannin) can be used as such or can be derivatised to obtain bio-based



building blocks. The latter can be further modified to obtain FiRs, based on their chemical structure and inherent thermal properties. To assess the use of bio-based materials as FiRs, it is necessary to inspect their composition and thermal behavior. Apart from this, bio-based materials should meet some other criteria as well, to be used as FiRs, that is, (i) these materials should bear sufficiently high thermal stability in compliance with their processing, (ii) their charring ability should be high, (iii) they should bear functional groups such as hydroxyls, carboxylic acids, amines, double bonds and others, that may undergo chemical transformations, and (iv) there should be inclusion of elements (P, N, Si) that are capable of introducing flame retardancy. Bio-based materials can be used by themselves as an ideal component of FiRs, or in combination with traditional FiRs such as P, N or with melamine, boric acid and also by chemical modifications.

### 2.1. Why biomolecules mentioned above are used in the field of FiRs?

Lignin is used as an additive to increase the fire retardance of polymers. At high temperatures, it gives the highest char yield. This char residue slows down combustion as it forms a protective layer. Lignin has been used in combination with boric acid, melamine, aluminum phosphate, urea and other FiRs. Proteins and deoxyribonucleic acid [DNA] are used in the field as both contain important elements, N and P, showing flame retardance. Both are capable to form films over textiles. The protein coating increases the burning time and slows down the burning rate. DNA, a natural intumescent FiR, contains C, N and P. Carbohydrates are used as charring agents as they contain oxygen. Starch is used as matrix and also as FiR coating in textiles through layer-by-layer technique. Chitosan as a carbon source is also used as FiR in textile coating by layer-by-layer technique. This technique improves FiR ability of the coated fabrics by declining their thermal decomposition and decreasing their burning time. Lipids such as fatty acids, vegetable oils, cardanol and others are also used as FiRs. Phosphorylation is the most frequently used method to introduce fire retardance in bio-based materials. Chitosan, lignin, vegetable oils, cardanol, and others have successfully undergone phosphorylation.

Past years have witnessed great research and development in this field. Several fire protection solutions have cropped up utilizing bio-based resources and complying with “Green Chemistry” principles. However, even with gigantic number of solutions available, it is not easy to assess which one is the most successful. In this context what should significantly be kept in mind is (i) overall performance of FiRs, (ii) environmental and health hazards associated with their processing, formulation and application, and (iii) cost effectiveness of raw materials used and processes involved. Vegetable oils [VO] are domestically abundant, cost-effective and non-toxic. They contain several functional groups that can be tailor-made by different chemical transformations through “greener” methods for different applications such as FiRs.

## 3. Vegetable oil based FiRs

VO can be modified by P, Si, halogens such as chlorine and bromine, to be used as FiRs. Such VO derivatives can be used as plasticizers for PVC (**Figure 7**). During thermal degradation, they provide carbon and acid sources that enhance flame retardancy by promoting char residue formation [4].



**Figure 7.** Phosphorus containing VO based derivatives, where (a-c) 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide groups containing soybean oil based derivatives, (d-e) diphenyl phosphine oxide containing sunflower oil based derivatives, (f-g) cashew nut shell liquid based derivatives, and (h-j) diethyl phosphate and chlorinated phosphate derivatives of castor oil [4].

In the synthesis of FiR polymers from VO, the advantage is taken of the presence of functional groups in VO such as double bonds, hydroxyl and ester groups which undergo derivatization reactions such as epoxidation, esterification, urethanation, alcoholysis and others (**Figure 8**). The inserted epoxide, ester, urethane groups or the alcoholized products are then modified accordingly by phosphorylation, silylation, boronation, halogenation and others resulting in FiRs [5]. The polymerization on double bonds can also be done by using styrene, divinyl benzene, dicyclopentadiene, and norbornadiene. Soybean and sunflower oils were reacted with acrylic acid and N-bromosuccinimide. The bromoacrylated products were then copolymerized with styrene, and this resulted in the formation of rigid FiR polymer [6, 7]. Bromine containing FiRs release hydrogen bromide during combustion, causing toxicity and corrosion. Therefore, P, Si and B containing polymers are significantly popular relative to those containing halogen because the combustion products they produce are non-toxic, while the latter release corrosives, pollute environment, erode instruments and are hazardous to human health.

VO derivatives have also shown dual behavior as they render flame retardancy and also plasticizing effect to polyvinyl chloride (PVC) materials, which find wide applications in packaging, pipes, toys, wire and cable. PVC materials show excellent mechanical and physical properties, not in neat form, but when combined with plasticizers, such as dioctyl phthalate [DOP] and dibutyl phthalate. However, there are disadvantages associated with the use of these plasticizers with PVC, such as diffusion of these plasticizers into surroundings, deterioration in the performance of PVC materials due to loss of plasticizers, and often being



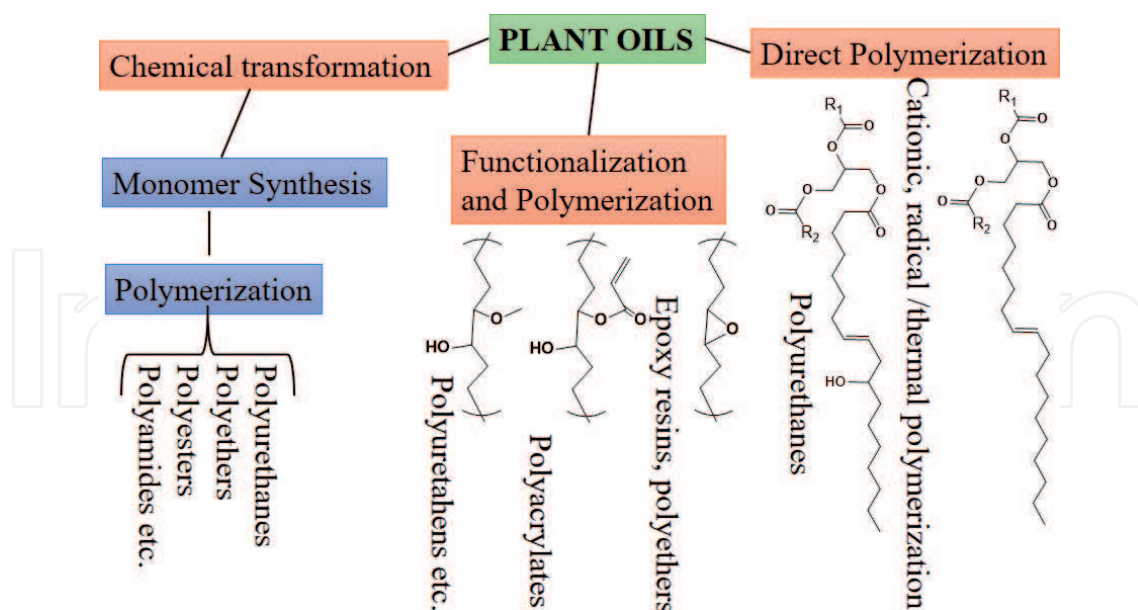
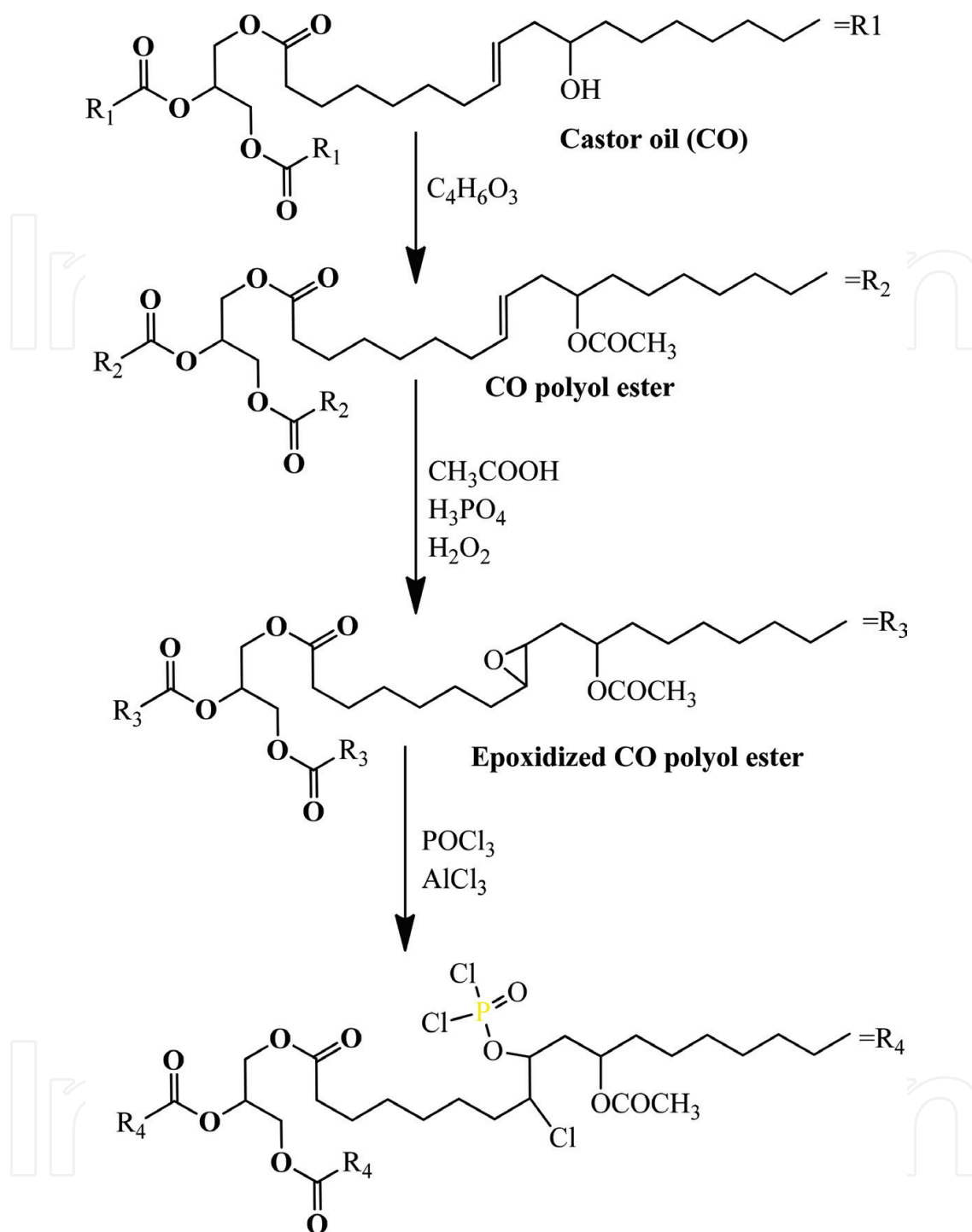


Figure 8. Chemical routes to produce VO derivatives [5].

susceptible to burning easily. The latter restricts their application in wire and cable that demand FiR properties. Thus, bio-based plasticizers that improve mechanical properties and flame retardancy (by supplying acid, carbon and gas source during thermal degradation of PVC materials) are welcomed [8–10].

VO-based FiRs and FiR plasticizers are prepared by different chemical transformations as mentioned above. Some of these have been discussed briefly in following sections:

*By epoxidation:* Epoxidation is carried out at the double bonds of VO. Epoxidized VO, followed by further derivatization such as ring opening of oxirane forming polyols, and also urethanation, produce FiRs. Castor oil [CO] was esterified at hydroxyl groups and then epoxidized at unsaturation producing epoxidized CO polyol ester, and the latter was treated with phosphorus oxychloride forming chloro phosphate ester of CO [CIPECO]. CIPECO was substituted in place of 50 wt% DOP for plasticizing PVC. CIPECO and DOP were blended with PVC in different ratio producing PVC films that showed high limited oxygen index [LOI] and improved thermal stability. During thermal degradation, the fatty acid chains of CO in CIPECO provided carbon source and the generated phosphorus containing components promoted the formation of char residual. Thus CIPECO improved plasticization and also flame retardancy of PVC (**Figure 9**) [4, 8]. CO was epoxidized at double bond and then the inserted oxirane ring was modified with diethyl phosphate in presence of triphenylphosphine producing phosphate ester, which was blended with PVC. The plasticized PVC showed high T<sub>g</sub>, improved thermal stability and high LOI values [11, 12]. Phosphorylated polyol polyurethanes [PU] were prepared by epoxidation of soybean oil followed by epoxide ring opening reaction with phosphoric acid, and the treatment of formed phosphorylated polyols with polymeric diphenylmethane diisocyanate [PMDI]. These PU showed flame retardancy same as commercial PU [13]. In another example, two types of polyols were prepared from rapeseed oil, one through epoxidation followed by ring opening reaction and the other one



### Chlorinated phosphate ester based on CO

**Figure 9.** Phosphorus and halogen containing FiRs from castor oil [8].

by transesterification with triethanolamine. PU foams were prepared by replacing 70% of petrochemical polyols by each of these polyols, adding expandable graphite [EG] as filler and then these formulations were treated with PMDI forming two-component PU. EG has stacked layers which are intercalated with acids (sulfuric, nitric, and acetic). Under the influence of

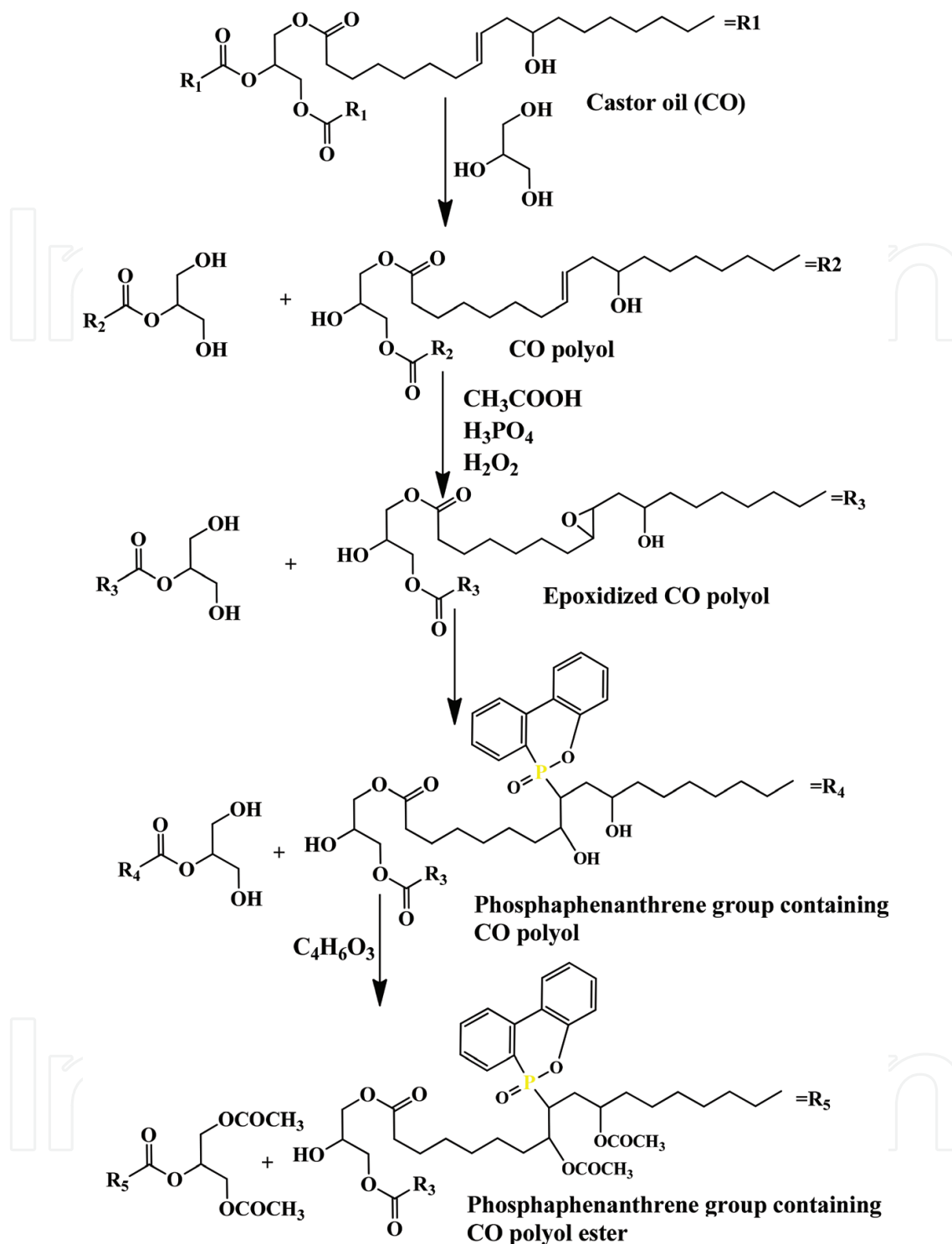


Figure 10. Phosphaphenanthrene containing FiR from castor oil [17].

high temperatures, EG reacts with acids releasing  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$  gases that cause expansion of graphite that behaves as physical barrier for heat and mass transfer. EG modified PU foams were characterized by flammability test by cone calorimeter to determine certain parameters (time to ignition, heat release rate, peak of heat release rate, time to peak of heat release

rate, total smoke release, maximum average rate of heat emission), and by combustion and thermal stability analyses. The inclusion of EG into VO-based PU foam reduced flammability, prolonged the combustion time, increased the average burning temperature and rendered overall good thermal properties and flame resistance to VO-based PU foam [7]. In another approach, CO was epoxidized, and phosphaphenanthrene [PPP] groups were inserted on epoxidized CO by oxirane ring opening reaction. The hydroxyl groups of CO and hydroxyl groups formed during oxirane ring opening reaction were esterified in the next step. This CO polyester with PPP groups was blended with PVC (partially replacing DOP). The modified CO polyester improved thermal stability of PVC by promoting the formation of char residue. The thermal degradation of PPP groups produces phosphorus rich layers that prevent oxygen and heat transfer, rendering PVC more thermally stable and flame retardant. Long fatty acid chains of CO form a rigid char skeleton preventing char from collapsing [14].

*By glycerolysis:* Glycerolysis of CO was accomplished with glycerol, in presence of sodium methoxide and triethanolamine forming monoglyceride and diglyceride of CO [15, 16]. The latter were further epoxidized at double bonds, and the epoxy ring opening reaction with diethylphosphate resulted in the formation of P containing flame retardant polyol. The flame retardant polyol formed PU foams in one shot process with PMDI. Such PU foams were analyzed with thermogravimetric analysis, flammability tests and cone calorimetric measurement, which showed excellent fire resistance performance of these PU, with only 3% P incorporation, compared to pure PU [15]. In another attempt, glycerolyzed products of CO, monoglyceride and diglyceride, were epoxidized and PPP groups were inserted in CO mono- and diglycerides by epoxide ring opening reaction. The hydroxyl groups of CO and those formed by epoxide ring opening were further esterified and these PPP-containing CO polyols were used as plasticizer for PVC, partially replacing with DOP (**Figure 10**). Thus plasticized, PVC showed high LOI (35.95%) values, improved thermal stability and reduced flammability [17]. Monoglyceride obtained by glycerolysis of Nahar seed oil, epichlorohydrin, bisphenol A and tetrabromobisphenol A were reacted together in an alkaline medium and then nanoclay was incorporated in different weight percentages (1, 2.5, and 5 wt%). These nanocomposites showed high LOI values ranging from 40 to 45. Flame retardance of these nanocomposites is related to the incorporation of nanoclay that acts as thermal insulator and mass transport barrier during thermal decomposition of epoxy, and also promotes char formation [18].

Thus, VO can be modified in several ways for their applications as FiRs. With numerous types of nanoparticulate systems and synthesis methods cropping up and the advent of newer techniques of analyses of FiRs, there is immense scope for utilization of VO as “green” FiRs.

## 4. Summary

With the presence of polymers in every sphere of daily life, the use of FiRs poses greater safety, health and environment concerns, also keeping in mind the demands for non-toxicity, cost effectiveness, level of performance and degree of “greenness” of the final product. The polymer

matrices are extensively diverse, and therefore no strategy claims as an ideal solution of fire/flame retardance. The research still continues on the topic in the quest for better and yet better.

FiRs. To some extent, bio-based FiRs do fill the gap.

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