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Chapter 1a: Polymer degradation and the matching of FR chemistry to degradation

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1. Thermal degradation of polymers

In fires, polymeric materials are consumed by flaming combustion which is a gas phase process. Thus the polymer must degrade to yield volatile combustible species to fuel the conflagration. To begin, this chapter first considers the various processes by which pure polymer systems degrade. Then any influence by which the presence of oxygen can affect these processes is discussed. The different structures of the various polymer types influence the end consequence of any decomposition and this will affect the resistance, if any, to combustion. At this point the polymer combustion cycle will be described.

Pure polymeric materials degrade via one or more of the following simple mechanisms.

- End chain scission, individual monomer units successively cleaved from chain end;
- Random chain scission, scissions occur at random locations along the polymer chain;
- Chain stripping, atoms or groups not part of the polymer backbone are cleaved off;
- Cross linking, bonds created between polymer chains.

Table1collates various examples of each of these mechanisms and the decomposition polymers obtained.

Mechanism	Examples of Polymer	Typical products
Random Chain Scission	Polyethylene,	Alkanes, alkenes, very little monomer.
	Polypropylene,	Alkanes, alkenes, very little monomer.
	Polystyrene,	Styrene monomer, dimer and trimer.
	...more generally	Monomers and oligomers
End Chain Scission	Polymethylmethacrylate	90 - 100% monomer
	Polytetrafluoroethylene	90 - 100% monomer
	.... more generally	Monomer
Chain Stripping	Polyvinyl chloride	Hydrogen chloride, aromatic hydrocarbons and char
	Polyvinyl alcohol	Water and char
	General	Small molecules and char
Cross-linking	Polyacrylonitrile Poly(oxy-m-xylene)	Char (and HCN) Char
	General	Much char, few volatile products

Table 1. Relative thermal Polymers and typical decomposition products for each generalised mechanisms of polymer decomposition [1]

Degradation is also influenced by the chemical structure of the polymer, i.e. straight chain, branched chain or cross linked. In addition, synthetic polymers fall into three physical types, each of which will decompose in a different manner when heated. These are thermoplastics, which will soften and melt before decomposing; thermosetting (cross-linked) which do not melt and decompose yielding char and evolving volatiles; elastomers which are rubber-like materials. In the main, these pure polymers degrade via 1st order kinetics. Madorsky [2] defined their relative thermal stability in terms of the temperature, T_h,at which their half-life equalled 30 minutes, see examples given in Table 2. From the T_h values, the effects of the various chemical structures on the thermal stability of these pure polymers can be deduced, see Table 3.

POLYMER	T_h (^oC)
Polymethylmethacrylate A (molecular wt. 1.5 x 10^5)	283
Polymethylmethacrylate B (molecular wt. 1.5 x 10^6)	327
Poly alpha-styrene	287
Polyisoprene	323
Polymethylacrylate	328
Polyethylene oxide	345
Polyisobutylene	348
Polystyrene	364
Polypropylene	387
Polydivinyl benzene	399
Polyethylene	406
Polymethylene	415
Polytetrafluoroethylene	509

Table 2. Relative thermal stability of selected polymers based on the temperature at which their half-life T_h is 30 minutes; data taken from Madorsky [2].

POLYMER	EFFECT ON THERMAL STABILITY	EXAMPLES	T_h (^oC)
Chain Branching	Weakens	Polymethylene	415
		Polyethylene	406
		Polypropylene	387
		Polyisobutylene	348
Double bonds in Polymer backbone	Weakens	Polypropylene	387
		Polyisoprene	323
Aromatic ring in polymer backbone	Strengthens	Polybenzyl	430
		Polystyrene	364
High molecular weight	Strengthens	PMMA B	327
		PMMA A	283
Cross-linking	Strengthens	Polydivinyl benzene	399
		Polystyrene	364
Oxygen in the polymer backbone	Weakens	Polymethylene	415
		Polyethylene oxide	345
		Polyoxymethylene	< 200

Table 3. Factors which affect the thermal stability of polymers; after Madorsky [2]

However, the intrinsic thermal degradation characteristics of any polymer may be influenced by impurity species present since polymers are rarely pure in the true chemical sense. Such impurities may include one or more of the following:

- impurities already present in monomeric feeds to polymerisation plants, although it may be generally stated that monomer purity is recognised as a critical variable by commercial polymer producers,
- polymerisation catalyst residues present in both addition and condensation polymers,
- products of degradation generated during polymerisation and processing, often of a thermally-derived origin. These may include products of thermal oxidation (see below),
- contaminants introduced during processing including atmospheric oxygen and metallic ions released from processing plant equipment.

These factors tend to be specific to each polymer type and its related polymerisation history and will be referred to below when discussing individual polymer degradation behaviour, if relevant. It is sufficient to state at this point that the consequences of these impurities is usually one of sensitising the overall degradation and gives rise to the slow thermal degradation and related deterioration in polymer properties often experienced when in use and exposed to service temperatures well below their normal rapid degradation temperatures as defined by T_h above. In many cases, when exposing a polymer to its maximum service temperature, its effective lifetime is determined by the length of the induction period for these low temperature degradation reactions to promote sufficient loss in properties as to render it useless for its intended purpose. Such induction times may be quantified in terms of times to embritlement, to lose 50% tensile strength or to change its character (e.g. colour) by a specified magnitude. Often, ageing at temperatures above the service life temperature but below the polymer melting point, for example, enables an apparent activation energy to be determined based on assumed Arrhenius law behaviour, from which service lives may be predicted, [3,4]. For these reasons, stabilising additives are usually included during the processing stages of any polymer and because of the complexity and often interrelated nature of these secondary reactions, such stabilisers may be required to minimise thermal degradation and oxidation in a concerted manner (see below).

In addition to the challenges posed by the presence of impurity, polymeric materials are rarely used in the "pure" or even stabilised state but are normally compounded with various compounds designed to enhance their properties, e.g. flexibility, mechanical strength, colour, stability, fire resistance, so that *-
3.-.-ok are focussed on the fire resistance aspect of modern every-day polymer materials, plastics and textiles as they are more commonly referred to.

2. Oxidative degradation

Polymer degradation is almost always faster in the presence of oxygen or air due to the accelerating reactions between oxygen and carbon centred radicals ($RO^{\cdot}$) released from the initial degradation products. These interactions with oxygen result in an increase in concentration of polymer alkyl radicals ($R^{\cdot}$) leading to higher levels of scission and cross-linked products. Also, fragmentation reactions of oxygen-centred radicals yield new oxidation products with structures not found under an inert atmosphere. These radicals can proceed to undergo abstraction, fragmentation and combination reactions both with the original polymer and other products from the decomposition. Such reactions can affect the polymer during processing, particularly if the temperature required is high, and also its performance during its end-use. For example, photo-oxidation reactions cause deterioration in the mechanical and physical properties of LDPE during the early stages of exposure. Antioxidants can be added to the plastic formulation to inhibit such effects. Antioxidants function by interfering with the radical reactions leading to polymer oxidation and degradation.

To understand these reactions, the so-called Bolland and Gee reaction scheme [5,6] and its subsequent developments has been applied to explain the chain reaction characteristics of both thermal and photo-oxidation of polyolefins in the main. The scheme (Scheme I) has been found to be a useful model for many other polymers comprising significant aliphatic character such as the aliphatic polyamides and polyesters and certain polyvinyls including poly(vinyl chloride) (PVC).

Scheme I: The general Bolland and Gee mechanism for the oxidation of polymers, RH

Initiation: $RH \xrightarrow{\Delta} R^{\bullet} + {}^{\bullet}H$

Propagation: $R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$

$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$

Termination: $R^{\bullet} + R^{\bullet} \rightarrow R\text{-}R$

$RO_2^{\bullet} + R^{\bullet} \rightarrow ROOR$

$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow$ Products

Chain branching: $ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$

3. Degradation of individual polymer types

When polymers are subjected to heat, it is generally the case that the weakest bonds will break first and these determine the overall character of the subsequent degradation pathways defined in section 1 above and exemplified in Table 1. Since flammability is associated with the availability and ease of oxidation of volatile degradation products, it is the degradation pathways that form volatiles which are of importance in the first instance. However, since cross-linking reactions give rise to eventual char formation and thus may minimise volatile formation, these reactions are essential in determining the potential of a polymer to be rendered flame retardant by condensed phase flame retardants that may favour these. In the discussion below, these reactions will be emphasised only within the overall contexts of the complex degradation mechanisms that most polymers exhibit when thermally degraded.

3.1 Thermoplastics

Polyolefins: For both polyethylene and its many copolymeric variants and polypropylene, the main thermal degradative routes follow initial random chain scission. These reactions are only slightly affected by the differences in physical structure such as crystallinity but are influenced by the presence of impurities present. However, it is largely true to say that while these may influence the processibility and long term stability of respective polyolefins, they have little or no effect on the flammability.

In the case of polypropylene, pyrolysis is dominated by initial chain scissions, usually at either carbon-carbon bond adjacent to the labile tertiary hydrogen atom in the repeat group $–CH_2-CH-(CH_3)-$. Research has shown that heating the polymer, including waste polypropylene, generates a mixture of quite clean hydrocarbon fuels [7, 8] and other valuable products such as lubricants [9, 10]. This fuel-forming tendency explains the high flammability of polypropylene and the difficulty of generating high levels of flame retardant properties while maintaining optimum polymer properties.

When heated under non-isothermal conditions, the maximum volatile product evolution temperature was 425°C for the isotactic PP to yield volatile products comprising dienes, alkanes, and alkenes. Furthermore, the hydrogen content of pyrolysis products obtained by flash pyrolysis at 520°C, indicates the magnitude of the flammability problem in term of its fuel-forming potential [11] The flammability of volatiles is further enhanced by the abundance of unsaturated less-volatile fuel fragments which behave as secondary fuel sources which decompose further [12].

The complete absence of cross-linking reactions prevents potential char-forming reactions being favoured in the presence of conventional condensed phase flame retardants and so the most effective flame retardants for polyolefins are usually bromine-based so that flame inhibition in the vapour phase is effected or intumescent-based where char-promotion arises from the flame retardant itself.

Aliphatic polyamides: The examples of nylons 6 and 6.6 will illustrate the challenges that these polymers create. The classical research into the thermal degradation occurred during the 1950-70 period and extensive reviews of this work include those by Kohan [13] and Peters and Still [14]. Essentailly all linear, aliphatic polyamide thermal degradation is influenced by two major factors:

(i) The strength of the weakest chain bonds around the amide group:

$$- CH_2 - CO - NH - CH_2 -$$
$$\uparrow \quad \uparrow \quad \uparrow$$

with bond cleavages occurring at the arrowed positions and preferential cleavage suggested to occur at the $- NH - CH_2 -$ bond [15, 16]. These occur randomly and give rise to the gaseous products, NH_3, CO and CO_2, low molecular weight fragments and subsequent degradation products from these latter. Of the simple gases, only CO is flammable but the volatiles generated from the smaller polymer chain fragments provide the major fuel components. The earliest nylon 6.6 pyrolysis work published showed the products to comprise cyclopentanone and various hydrocarbons and this was supported by later work [13] although the former was unique to nylon 6.6 and not nylon 6. Thermal decomposition of nylon 6 involves the depolymerisation to its monomer caprolactam which is not only faster at higher temperatures but is volatile at temperatures above.

Thermal lability of aliphatic nylons in general is influenced by the potential for ring-forming and this is particularly the case with nylon 6.6 in which the adipate repeat enables formation of a six-membered

intermediate to form along the polymer chains with eventual formation of cyclopentanone and its derivatives [18 (i)].

(ii) The tendency of certain aliphatic polyamides to form 3-dimensional structures leading to gel formation. Nylon 6.6 is particularly prone to this and this explains why melt extrusion processes often require more interruptions because of potential gel blockages than is the case with nylon 6, for example. Nylon 6.6 gels typically after 6 hours at 305^{o}C while nylon 6 may be heated for up to 10 days at 281^{o}C before it gels [13]. While gel formation mechanisms are not well-understood, in nylon 6.6, the formation of cyclopentanone derivatives and their subsequent reaction products are believed to be involved.

It is thus apparent that the overall flammability of the simple nylons is determined by their relative propensities to shrink and melt away from an ignition source in the first instance followed by the nature of the volatiles formed, which if ammonia and carbon dioxide are significantly present, will have a reduced fuel value. Any flame retardant strategy may thus address this volatile formation or perhaps more interestingly accelerate gel formation which could lead to a significant char-forming character. Unfortunately, to date, few successful flame retardants have been successfully commercialised for nylons 6 and 6.6 partly because of the reactivity of nylon melts to bromine-containing retardants and also the adverse effects of phosphorus-containing species on the molecular weight of melts during processing. Levchik and Weil [18(ii)] have reviewed this whole area and show that certain melamine salts in particular show promise.

Polyesters: The principal linear polyester is poly(ethyleneterephalate) (PET) and so this will be the chosen exemplar. Studies of its thermal degradative behaviour mirror those of the aliphatic polyamides above in that during the commercial development of PET during the 1950's and 1960's, the basic research work was undertaken then [14]. While some cross-linking tendency has been identified [19], in the main, random chain scission dominates thermal degradation with the major product being acetaldehyde being formed at temperatures up to 290^{o}C along with smaller amounts of CO, CO_2 and ethane and very small amounts of other fuels such as methane and benzene [20]. Straus S and Wall L A, *J Res Nat Bur Stds.*, **60**, 39 (1958).

A simplified version of the primary stage appears to be:

$$-C_6H_4.CO.O.CH_2.CH_2.O.CO- \xrightarrow{\Delta} -C_6H_4.CO.OH +$$

$$-C_6H_4.CO.O.CH_2=CH_2 + HO.CO.C_6H_4.- \rightarrow CH_2=CH_2.O.CO.C_6H_4.- + CH_3.CHO + -C_6H_4.CO.O.CO.C_6H_4.-$$

in which it is seen that acetaldehyde is formed as the major initial flammable volatile. Action of further heat causes polymerisation of the vinyl ends coupled with loss of CO and CO_2 as the anhydride links undergo further scission.

It is evident that any flame retardant must counteract the effect of or reduce the amount of the acetaldehyde formed. While the actions of bromine- and phosphorus-containing species have achieved varying degrees of success, no successful flame retardant to date has managed to confer a significant char-forming character to the degradative mechanism and this is perhaps an indication in the challenges involved with effectively flame retarding linear polyesters in general.

Polyacrylonitrile: Most commercial polymers comprising acrylonitrile (AN) are copolymeric and those containing the highest levels of AN monomer, usually 85wt% or more, are for use in fibre end-uses including carbon fibres, where they are major precursors. It is as a consequence of their importance as carbon fibre precursors that most research on the thermal degradative and oxidative processes associated with acrylonitrile copolymers has focussed in this area and took place over the 1960-1980 period in the main [14, 21, 22]. It is generally accepted that the pyrolysis of AN-containing copolymes of this type are dominated by the behaviour of the AN monomeric unit itself and that this undergoes a cyclisation reaction accompanied by an intense exotherm either in an inert atmosphere or in the presence of oxygen [23] This gives rise to a so-called "ladder" structure as opposed to the random chain scission of chains into potential volatile product formation. In carbon fibre production, this cyclisation is closely controlled by heating in an oxygenated atmosphere to produce so-called oxidised acrylic fibres which have acceptable fibre properties in their own right [24]. Furthermore, because they are highly carbonised, these fibres have a high inherent fire resistance with limiting oxygen index (LOI) values of 50-55 vol%. Subsequent heating in an inert atmosphere converts these fibres into carbon fibres having an essentially graphitic structure.

In parallel, however, has been the exploitation of fibre-forming acrylic copolymers in the textile area where they produce fabrics having similar levels of flammability as cotton with similar limiting oxygen index values of about 18 vol%. This high level of flammability at first sight appears to be at odds with the cross-linking, carbonising reactions observed in carbon fibre production. However, work in our own laboratories [25]showed that the pyrolysis mechanism is both temperature and heating rate dependent. Under the slow heating conditions and temperatures up to 400^{o}C associated with carbon fibre production, the cyclisation and cross-linking reactions prevail whereas under the high heating rates and temperatures above 400^{o}C associated with burning, volatilisation and fuel-forming reactions predominate.

It therefore becomes evident that in order to flame retard polymers containing high levels of acrylonitrile, this tendency to volatilise at high heating rates must be overcome. In commercial terms this has proved to be impossible to date and the only successful AN-containing, fibre-forming polymeric the group of modacrylics, contain between 35 and 85% AN with the other comonomers being a halogen-containing species such as vinyl chloride or vinylidene chloride. These release chlorine atoms into the flame on heating and so act as vapour phase flame retardants. However, at the experimental level, we have also shown that the volatilisation reactions may be suppressed in favour of char formation if ammonium polyphosphate and similar flame retardants are introduced, but as yet, these have not been commercialised [26].

Polystyrene: Polystyrene is well known for a multitude of general purpose applications. Derivatives with superior properties for particular applications, in

particular, acrylonitrile—butadiene-styrene (ABS) and rubber-modified, high impact polystyrene (HIPS) are used to replace PS or used in conjunction with it. Untreated PS decomposes above 300ºC producing mainly styrene monomer plus lesser amounts of the dimer, trimer and tetramer all of which are highly flammable as a consequence the LOI value for PS is 19.0 vol.%. The mechanism is dominated by chain scission, depolymerisation, intramolecular hydrogen transfer and bimolecular termination [1, 27]. The main products are styrene monomer and its oligomers plus benzene and toluene. As would be expected from the aromatic nature of the PS structure, the principal flame retardant mechanism occurs in the condensed phase facilitating char formation. Post-polymerisation modification to flame retard PS is easily achieved via electrophilic aromatic substitution of suitable flame retardant groups onto the phenyl rings. Successful methods include boronation [28], sillation [29] and phosphorylation [30]. PS, ABS and HIPS are more often flame retarded using additives which are cost effective and easy to process. Various halogenated-flame retardant/ATO combinations which evolve flame inhibitors under fire conditions are often used.

PolyVinylChloride: Loss of the flame inhibitor HCl, via autocatalytic chain stripping, occurs from about 100ºC. Thus PVC has its own 'in-built' fire retardant which is why PVC initially found extensive use in hazardous situations such as coal mines. This reaction yields other products which can be involved in other reactions such as cross-linking [31]. The conjugated double bonds resulting from the loss of HCl gives rise to aromatic structures, e.g. benzene, that burn producing significant quantities of hazardous smoke. Extensive studies have been undertaken to identify efficient smoke suppression systems for PVC, in particular those by Starnes [32] and Carty [33]. Alternatively, the polyene structures can continue to undergo cross-linking to produce the much less flammable char.

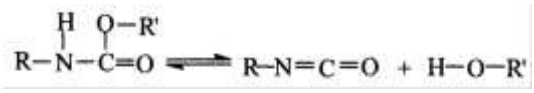
EthyleneVinylAcetateCopolymers: EVA is a widely used material, particularly as a low cost, zero-halogen sheathing material in the electric cable industry. EVA is known to form a protective layer which can inhibit combustion [34]. TG/FTIR studies by Maurin, Dittert and Hussain [35] showed that heating of EVA composites resulted in a two step decomposition over the ranges 360-450ºC and 450-550ºC. The first step is due to evolution of acetic acid and the second a mixture of 1-butene, carbon dioxide, ethylene, methane and carbon monoxide. A recent study [36] of the of the mechanism and kinetics of PVA and EVA degradations has shown that the deacetylation process leaves a highly unsaturated polyene-type residue. The deacetylation of PVAc is autocatalytic but upon incorporation of ethylene entities into the polymer backbone, this autocatalysis disappears. Between 400-500ºC, the polyene will degrade further by chain scission reactions in inert conditions or aromatise in an oxidative environment into a char, and eventually CO_2 above 500ºC. Under inert conditions, deacetylation is endothermic but in the presence of oxygen, large exothermic effects are found for each degradation step. This indicates the occurrence of additional oxidation reactions during deacetylation, an important reorganisation of the polyene structure prior to char formation and oxidation of the latter to CO_2.

3.2 Foams: Thermal degradation of foams is no different from that of the solid polymer except in that the foam structure imparts superior thermal insulation properties so that the decomposition of the foam will be slower than that of the solid polymer. Almost every plastic can be produced with a foam structure but only a few

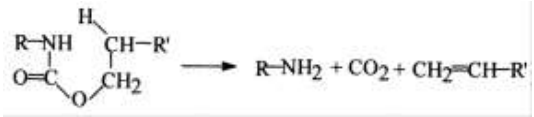
are commercially significant. Of these flexible and rigid polurethane foams, which have urethane links in the polymer chain, are the most important. The thermal decomposition products of polyurethane will depend on its composition which can be chemically complex due to the wide range of starting materials and combinations which can be used to produce them and their required properties. Basically these involve the reaction between isocyanates, such as toluene 2,4 and 2,6 diisocyanate (TDI) or diphenylmethane 4,3 diisocyanate (MDI), and polyols. If the requirement is for greater heat stability and reduced brittleness then MDI is favoured over TDI.

Urethane linkages tend to dissociate above about 200 ^{o}C. Fabris [37] indicated that urethanes from many isocyanates and primary and secondary alcohols begin to decompose at 150-200 ^{o}C proceeding at a measurable rate above this range. Urethane bonds decompose by the following three mechanisms:

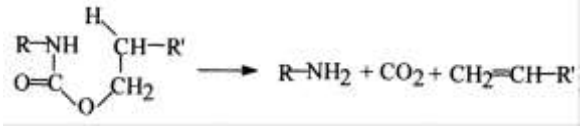
reversal to the original isocyanate and alcohol:



formation of the primary amine, olefin and CO_2 through the intermediate state of a six-membered ring:



formation of the secondary amine and CO_2through the intermediate state of a four-membered ring:



Wooley [38] used GC/MS to investigate the thermal decomposition of commercial TDI-based flexible foams under nitrogen. The degradations began with urethane bond scissions at 200-300^{o}C to yield relatively non-volatile polyol components and nitrogen rich volatiles. The latter were termed ‘yellow smoke’ and appeared to be polymerised or condensed forms of TDI with some free TDI. At higher temperatures, further degradation of the polyol residue occurs to yield small organic species.

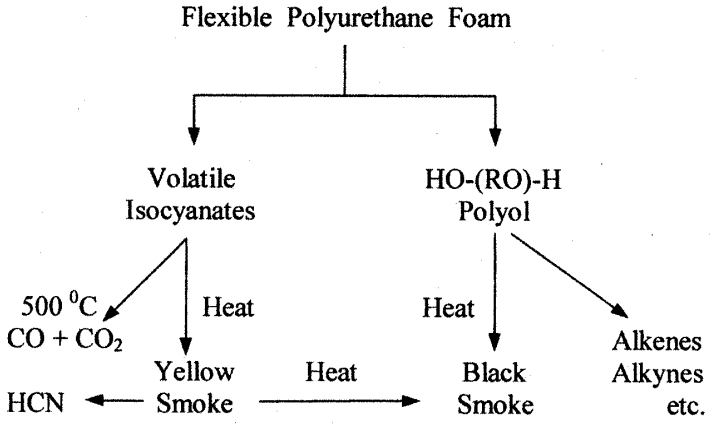
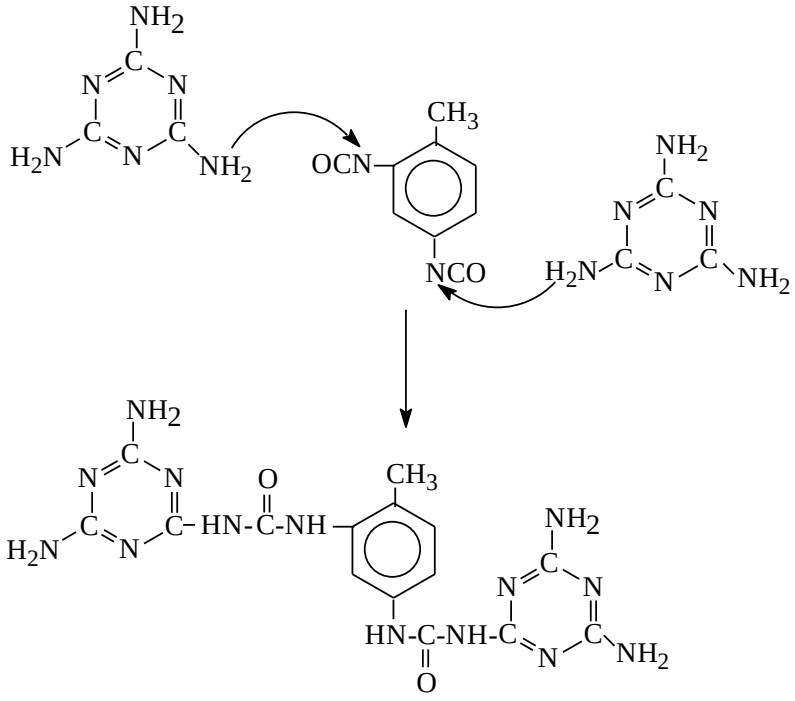


Figure 1. Thermal degradation of flexible polyurethane foam [38].

The major application of PU foam is for upholstered furniture. Because of their large surface area and high air permeability, polyurethane foams are highly flammable. As a consequence it is essential that flame retarded PU foam be used in upholstered furniture [39]. Chlorinated phosphate esters are widely used to flame retard PU foams. These have the disadvantage that they can increase smoke formation. An additive which can effectively trap the volatile isocyanate evolved during the thermal decomposition of the foam can lead to a reduction in the smoke and toxic gas yields. A common example is melamine. Price and Yan Liu [40], studied the reduction of smoke due to the presence of melamine in polyurethane foams. Overall, the interaction between melamine and the released isocyanate fraction arising from the decomposition of polyurethane foam is considered as the main reason for the smoke-suppression of melamine. Although no reaction is believed to occur between melamine and TDI during the manufacture of polyurethane foam at processing temperature around 100 °C, at higher temperatures interaction may occur. The melamine $–NH_2$ group is very reactive towards an isocyanate (–NCO) group. Thus, the reaction shown below would be expected to occur when temperature is over 250 °C. The polymeric structure so formed would reduce the amount of aromatic smoke precursors volatilised, thus reducing the smoke released. This type of structure would degrade to a char which will protect the remaining foam.



Thermosets: Thermoset resins covers an extremely wide range including phenol formaldehyde polymers, aminopolymers, polyurethanes, epoxies and thermoset polyesters which include the alkyd and unsaturated vinyl ester resins. Of special interest at the present time are those that comprise the resin component of fibre-reinforced composites which are finding increasing use in commercial and defence sectors where fire resistance is of paramount importance. Typical resins used here are those listed in Table 4 along with typical, respective LOI values in descending order of increased inherent fire resistance.

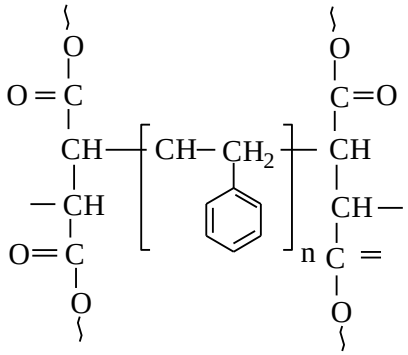
Table 4: Thermoset resins used in composites

Resin type	**LOI, vol%**
Polyester	20-22

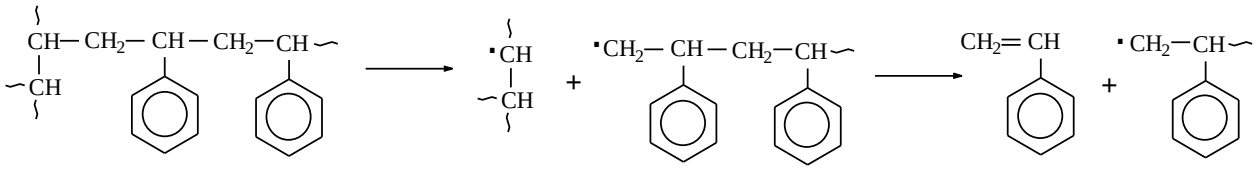
Vinyl ester	20-23
Epoxy	23
Phenolic	25
Polyaromatic melamine	30
Bismaleimide	35

Their general thermal stability and flame retardancy have been recently reviewed [41]

Polyester resins **:** Polyesters are probably the most commonly used of polymeric resin materials and consist of a relatively low molecular weight unsaturated polyester chain dissolved in styrene, which on curing forms cross-links across unsaturated sites in the polyester. The typical formula for a resin is:



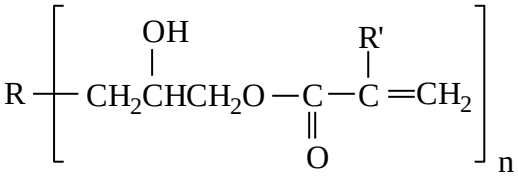
Most polyesters start to decompose above 250 ^{0}C, whereas the main step of weight loss occurs between 300 and 400 ^{0}C [42]). During thermal decomposition, polystyrene cross-links start to decompose first and styrene is volatilized.



The linear polyester portion undergoes scission similar to thermoplastic polyesters, undergoing decarbonylation, decarboxylation or splitting off of methylacetylene.

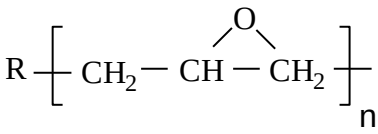
Because of the ease of formation of these flammable pyrolysis products, polyesters have LOI values of 20-22 vol% (see Table 4) and hence, burn readily and because of the styrene content, give heavy soot formation. Because these resins are cured at room temperature, then bromine-containing flame retardants which would decompose in melt-processed, thermoplastic polymers may be used with effectiveness here.

Vinyl ester resins**:** These are mainly derived from reaction of an epoxy resin e.g., bisphenol A diglycidyl ether, with acrylic or methacrylic acid. Their general formula is:

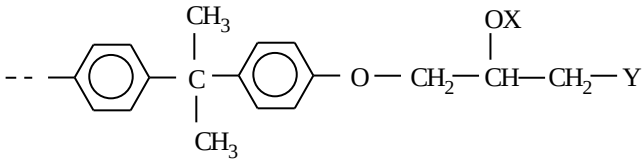


where R is any aliphatic or aromatic residue and R' is typically either H or CH_3.
Like unsaturated polyesters they are copolymerised with diluents such as styrene using similar-free-radical initiators. They differ from polyesters in that the unsaturation is at the end of the molecule and not along the polymer chains. Their burning behaviour falls between that of polyester and epoxy resins (LOI = 20-23 vl%, Table 4).

***Epoxy resins*:** These resins, extensively used in the aerospace industry, consist of an epoxy resin component, often based on epichlorohydrin and a curing agent and comprising the epoxy or glycidyl group shown below:



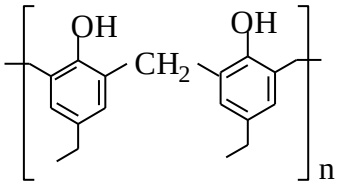
where R is any aliphatic or aromatic residue. This group will react typically with phenolic –OH groups and Bisphenol-A type resins to yield a general structure shown as



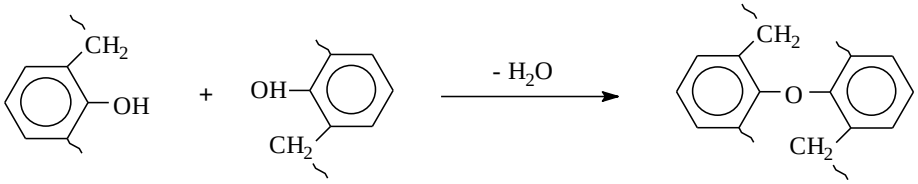
where X can be H and Y depends upon the structure of curing agent. This yields a relatively thermally stable structure with weakest bonds at the ether linkage, –O–.
During early stages of thermal degradation the reactions are mainly non-chain-scission type, whereas at higher temperatures, chain-scissions occur [43]. The most important non-scission reactions occurring in these resins are the competing dehydration and dehydrogenation reactions associated with secondary alcohol groups in the cured resin structures. The main products are methane, carbon dioxide, formaldehyde, and hydrogen.
During chain scission reactions the aliphatic segments break down into methane and ethylene (and possibly propylene), acetone, acetaldehyde, and methane (and probably carbon monoxide and formaldehyde) all of which are flammable. From the aromatic segments of the polymer, phenol is liberated. For phthalic anhydride - cured resins, phthalic anhydride is regenerated together with CO and CO_2, benzene, toluene, o-and p-cresols and higher phenols.
However, the flammable volatiles outlined above are produced only in relatively small quantities and this, coupled with their cross-linked and related char-forming character, ensures that epoxy resins are less combustible than polyester resins with higher LOI values in the range 22-23 vol%.

Phenolic resins: Reaction of phenol with less than equimolar proportions of formaldehyde under acidic conditions gives so-called novolac resins containing

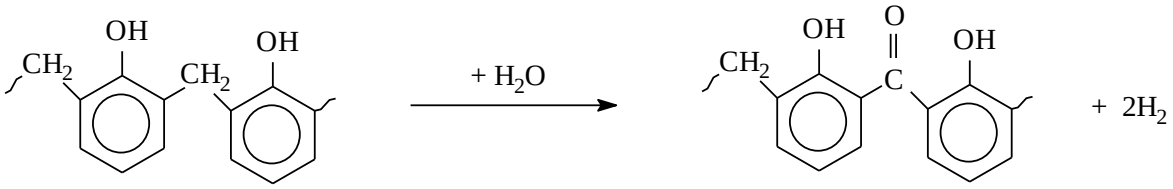
aromatic phenol units linked predominantly by methylene bridges. These are thermally stable and can be cured by cross-linking with formaldehyde donors such as hexamethylenetetramine. However, the most widely used phenolic resins for composites are resoles manufactured by reacting phenol with a greater than equimolar amount of formaldehyde under alkaline conditions. Resoles are essentially hydroxymethyl functional phenols or polynuclear phenols with the general formula:



Phenolics have LOI values of 25 vol% or so and this high level of inherent flame resistance is associated with the general thermal stability and often means that no further flame retarding is necessary to create composites having required performance levels. During heating, water is generated chemically during the first step of thermal degradation primarily because of phenol-phenol condensation by reactions of the type:

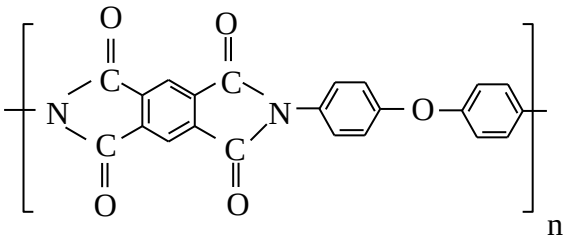


The released water then helps in the oxidation of methylene groups to carbonyl linkages [42], which then decompose further, releasing CO, CO_2 and other volatile products to yield ultimately char.



In the case of highly cross-linked material, water is not released until above 400 ^{0}C, and decomposition starts above 500 ^{0}C. as confirmed using DTA [44]. The amount of char depends upon the structure of phenol, initial cross-links and tendency to cross-link during decomposition. The main decomposition products may include methane, acetone, carbon monoxide, propanol and propane.

***Maleimide and polyimide resins*: T**heir chemistry is often complex with a general formula for polyimide resins represented by:



The aromatic structure of polyimides in particular ensures that they are thermally resistant and hence characterised by high char formation on pyrolysis, low flammability (LOI > 30 vol.%) and low smoke production.

3.4 Natural Polymers

Cellulose: Cellulose, either as the major component of wood or as the major textile fibre cotton, is frequently involved in fires. Thermal degradation of cellulose results in the evolution of highly combustible volatiles which will be consumed in a flame if ignited. Flame retardant treatments need to affect this degradation process either by reducing the extent of volatile escape in favour of less flammable residue formation or evolve flame inhibitors such as $Br^{\cdot}$ or $Cl^{\cdot}$ species. Cellulose consists of long, linear chains of β-1,4-*D*(+)-glucopyranose units linked by 1,4-glucosidic bonds.The cellulose molecule is not planar but has a screw axis, each cellulose unit being at right angles to the previous one. Free rotation about the C-O-C link does not occur due to steric effects in the solid state. The degradation of wood will not be discussed here because in addition to cellulose, wood and plant cells contain hemicellulose and lignin which further complicate the degadation process. Because of its wide usage in the textile and other industries, as a source of alternative fuels, the pyrolytic decomposition of cellulose has been extensively studied [45]. Whilst other more detailed mechanisms have appeared in the literature [46,47], the basic mechanisms proposed are all in line with that first suggested by Bradbury and Shafizadeh [48] who suggested that a precursor step in which an 'activated' cellulose species Cellulose* which then undergoes further reaction depending on the temperature regime as presented in Fig. ?

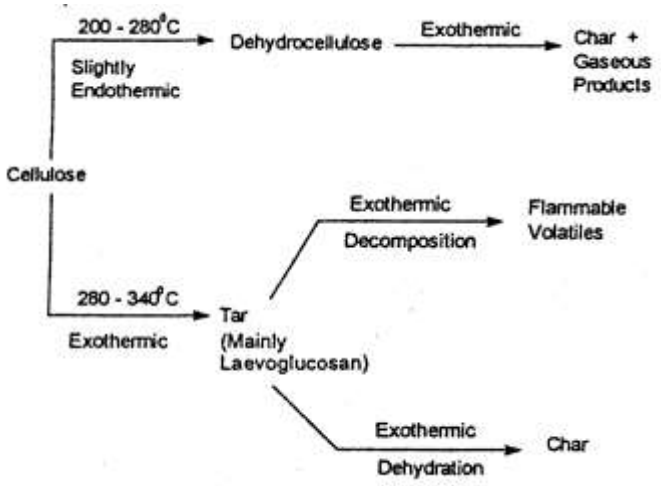


Figure 2. Basic scheme for cellulose degradation process; after Bradbury et al [48].

Whilst there is controversey as to whether or not this Cellulose* species exists or not, experimental evidence for the Cellulose* species was obtained by Price et al [49] who suggested it could be free radical in nature. At lower temperatures, oxygen plays a dominant role is cellulose degradation, pyrolysis is faster in an oxidative atmosphere than in an inert one [50] Oxygen catalyses the formation of both volatiles and char promoting reactions [51] At higher temperatures, the degradation products are little affected [50].

Proteins: **Protein polymers:** Proteins or poly(α-amino acids) feature the amide link common to the polyamides and may, in fact, be considered to be α-carbon substituted nylon 2 variants. Thus their potential thermal degradation behaviour might be expected to be similar to that of the aliphatic polyamides defined above. However, the α-substituents or substitutent-R groups are often quite reactive because of their functionalities and so these will significantly influence, if not determine, the thermal degradation behaviour and potential flammability.

Commercial protein polymers were first developed during the early 20th century, a prime example being casein from milk. On reaction with formaldehyde this gives a polymer which found much use as a synthetic horn or tortoiseshell material and it still has some commercial presence in milk-producing countries like New Zealand. However, the most important protein polymers that require flame retardation are those associated with textiles with silk and wool as the principal examples. Whereas the aesthetics of silk define its commercial importance and the effect that most proprietary flame retardant treatments have on this fibre precludes it from being used in fire resistant textiles, there has been recent commercial interest in its use in executive jet aircraft interior décor in which, as with normal commercial airliners, stringent fire standards are demanded. We have published work in this area to demonstrate the flame retardant challenges to be overcome [52]. Silk comprises 16 α-amino acids of which glycine (R=H), alanine (R=CH_3) and serine (R= CH_2OH) are the major comonomers present. When heated, silk starts to decompose above 250ºC and forms a char. This charring characteristic is probably largely influenced by the dehydrating and cross-linking tendency of the hydroxyl group within the serine -CH_2OH α-substituent. Charring can be increased by application of phosphorus-containing species as might be expected given this assumed chemistry [53]. The natural fibre LOI value is 22-23 vol% reflecting this higher char-forming tendency than the simple aliphatic nylons which have LOI values of about 21 vol%.

Wool fibres and fabrics, however, have significantly greater commercial applications in products such as protective clothing and contract upholstery where high levels of fire resistant performance are demanded. Wool, while also comprising a large number (18) of α-amino acids, some of which are in common with silk, is uniquely identified by the presence of sulphur-containing α-substituents of which cystine (R = -CH_2-S-S-CH_2-) comprises nearly 10 wt% of the whole fibre and provides cross-links between adjacent polypeptide chains. This high sulphur content (3-4 wt%) coupled with the

high nitrogen content (15-16 wt%) present in both chain and side groups contributes to the inherently low flammability of wool. The fibre also contains about 15 wt% of adsorbed moisture under normal atmospheric conditions and LOI values are in the 25-26 vol% range. When wool is heated, it starts to give off its adsorbed moisture at 100°C and above and then starts to thermally degrade above 200°C giving off gases which include H_2S alongside char formation [54]. The relatively non-flammable volatiles coupled with char formation are encouraged by cross-linking and dehydrating tendencies of the α-substituents present. The overall action of these is to give a relatively high ignition temperature of 570-600°C and low flame temperature of about 680°C. The cystine disulphide link is particularly interesting here since it has highly reducing properties and so encourages subsequent oxidation by oxygen during the pyrolysis/combustion process. Pre-oxidation of the cystine to cysteic acid ($R=CH_2.SO_3H$) residues actually improves flame retardancy.

3.5 High temperature resistant polymers

These tend to be highly aromatic in character with rigid polymer chain backbones to yield polymers having very high second order transition values, absence of achievable melting transitions and decomposition temperatures rarely below 400°C. It is generally the case that the lower the aliphatic content, the lower is the hydrogen to carbon ratio and hence the lower is the flammability of any polymer. Aromatic chain polymers generally have H/C ratios < 1 and so their ability to generate volatile and flammable degradation species at temperatures below 500°C or so is very limited. Consequently they have LOI values generally above 30 vol.% and are generally deemed to be sufficiently flame resistant for the applications for which they are selected.

Table 5 illustrates a selection of the more common high temperature, aromatic-structured polymers used for producing heat and flame resistant, high performance fibres and their related thermal transitions and LOI values [55].

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Table 5: Thermal transitions and LOI values for selected aromatic, high temperature resistant fibre-forming polymers [55].

Fibre genus	Second order temperature, °C	Melting temperature, °C	Onset of decomposition, °C	LOI, vol %
Phenol formaldehyde: Novoloid	NA	NA	>150	30-34

m-Aramid	275	375-430 (decomposition)	425	28-31
p-Aramid	340	560 (decomposition)	>590	29-31
Copolymeric p-aramid	-	-	500	25
Arimid (P84)	315	-	450	36-38
Aramid-arimid	<315	-	380	32
Semicarbon	NA	NA	NA	55
Polybenzimidazole, PBI	>400	NA	450/air;1000/inert	>41
Polybenzoxazole, PBO	-	-	650;>700/inert	68

Notes: NA=not applicable; (decomposition)= with decomposition

These polymers may be compared with the more detailed discussion of thermal degradation pathways for phenol-formaldehyde resins in Section 3.3 above which more fully explains the reasons for generally low flammabilities in such highly aromatic structures. This same polymer in its novoloid form is commercially available as a fibre with properties defined in Table 5.

Addition of flame retardant species to these polymers is rarely undertaken since not only are they intractable during processing but also the added value in terms of improved fire resistance is usually difficult to observe. The high costs of these polymers also negates the use of additional additives unless a real benefit is to be achieved.

4. Polymer Fire

Figure 1 is a schematic cross-section of a polymer fire indicating the important reaction zones.

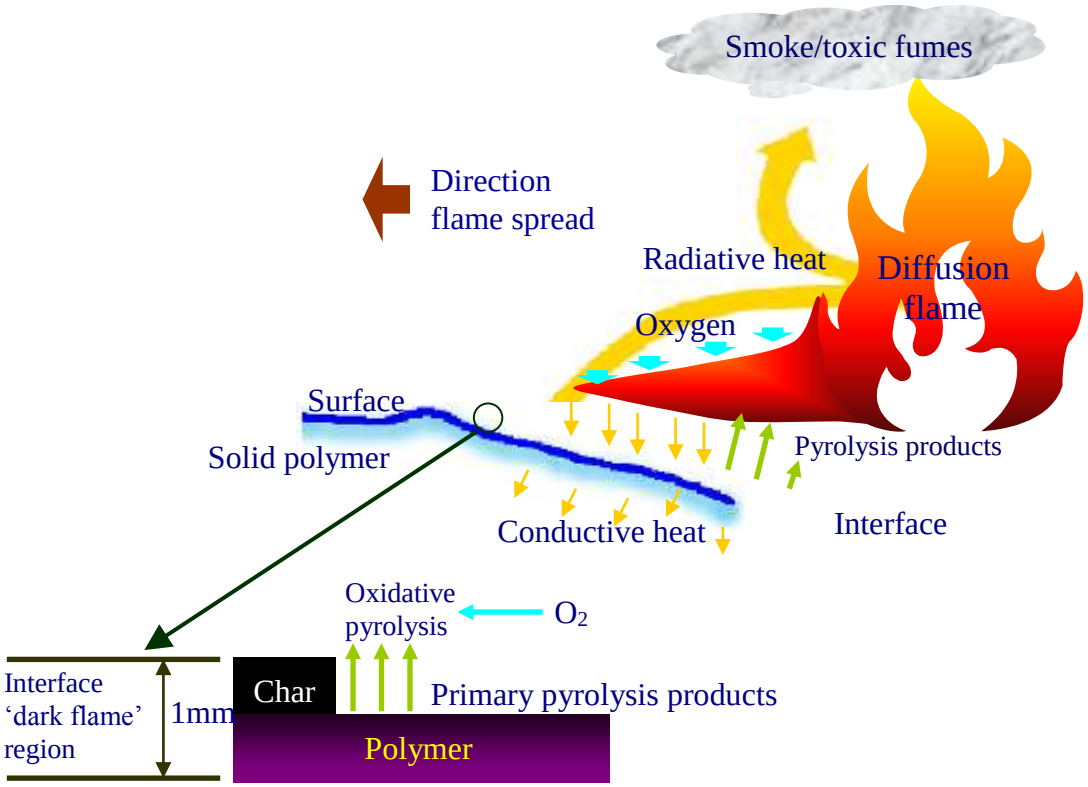


Figure 3. Schematic representation of a burning polymer.

The flame is fuelled by combustible pyrolysis products escaping from the polymer surface due to heat being conducted from the flame in contact with the polymer surface and also radiated from the flame. The latter is the significant cause of flame spread and this process is modelled by the cone calorimeter [56]. The oxygen required to sustain the flame combustion diffuses in from the air environment. Various solid particles escape from the flame as smoke which is accompanied by gaseous species some of which can be toxic [57]. The significant polymer degradation reactions occur within a millimetre or so of the interface between the flame and the solid polymer. Here, the temperature is high enough for condensed phase degradation reactions to occur. These involve the polymer and any additive systems included in the polymer formulations. Volatile species formed escape into the flame whilst heavier species remain to undergo further reaction and may eventually degrade leaving a char. This is where the significant condensed phase chemistry occurs. Experimental studies of this region have been undertaken by Price [58] and Marosi [59].

5. Polymer combustion cycle

An account of the polymer combustion cycle is simplified by reference to the schematic representation given in figure 2. In order for a polymer material to undergo flaming combustion it must first degrade to evolve combustible volatiles which escape and mix with an oxidative atmosphere. Provided the temperature is above the ignition temperature or a suitable ignition source, such as a spark, is present this mixture will ignite. The flames will yield gaseous products some of which may be

toxic, smoke and fumes as well as heat. Some of the heat will be conducted or radiated back to the original polymer to cause further degradation. Provided this heat is sufficiently intense, a combustion cycle will be established as indicated schematically in the figure.

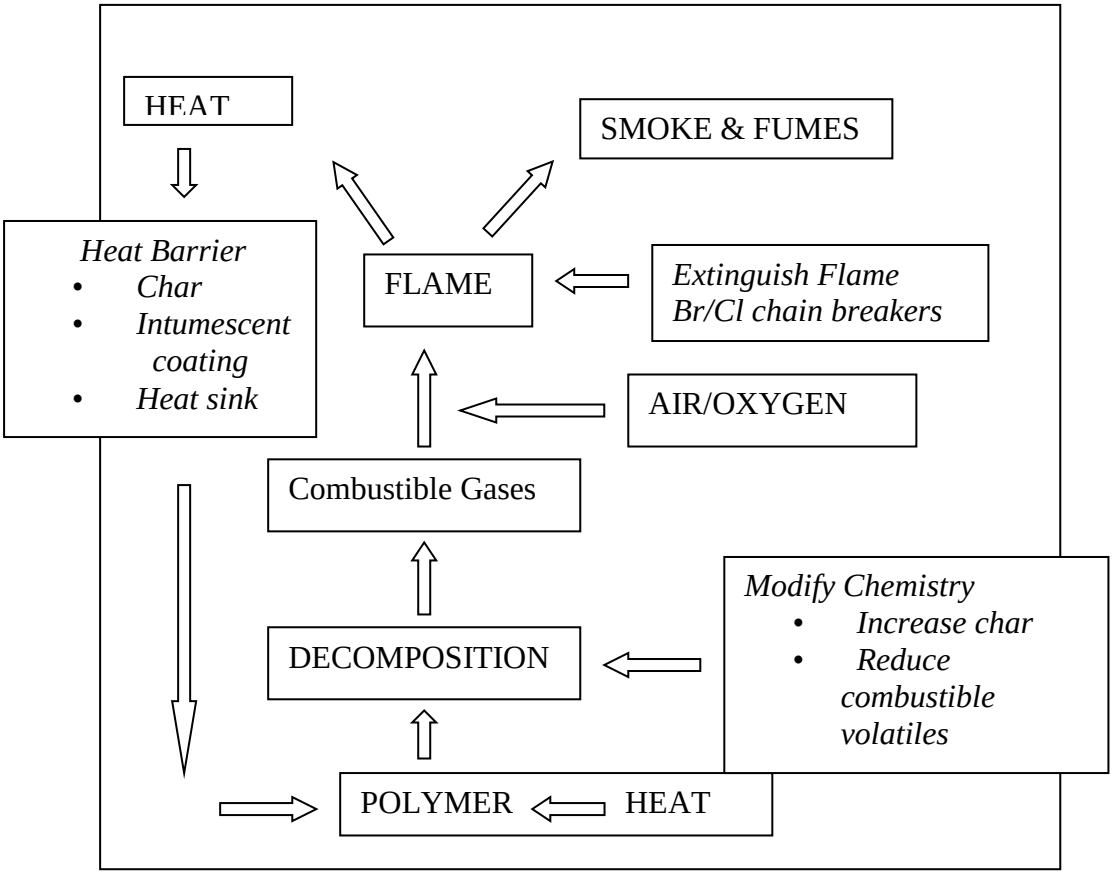


Figure 4. Schematic representation of the polymer combustion cycle; main approaches to flame retardancy are shown in italics.

6. Flame retardance

Most plastics and textiles are organic and thus vulnerable in a fire situation. A major concern of their manufacturers is, therefore, to render their products resistant to ignition or, if they are ignited, to burn less efficiently so that their rate of heat release is significantly reduced. The approach to achieving this is termed 'flame retardance'. Unless the polymer is inherently flame retarded, the various approaches indicated in figure 4 can be used to reduce the fire threat of such materials. One method is to prevent access of oxygen to the flame, another is to introduced flame inhibitors such as halogen atoms, $Cl\cdot$ and particularly $Br\cdot$, or phosphorus into the flame. This can be accomplished by including additives, in the material's formulation, which release these flame inhibitors if the material is exposed to temperatures approaching the ignition temperature. An alternative approach is to introduce suitable chemical groups into the polymer structure, so called 'reactive flame retardants', which provide the same effect. The combustion can also be halted by reducing the heat flow back to the polymer thus preventing further degradation. This can be achieved by the introduction

of a heat sink such as aluminium oxide trihydrate ($Al(OH)_3$) or magnesium hydroxide ($Mg(OH)_2$) which decompose with a large endothermicity. Formation of a heat barrier, e.g. either a char or intumescent barrier as a result of exposure of the material to a fire is another successful method. Finally there is the option to modify the polymer degradation chemistry so that the amount of flammables released is below the level required to fuel the flames whilst at the same time increasing the less combustible char formation. The char has the beneficial effect of forming a barrier between the polymer surface and the flame. It is during these latter condensed phase processes that polymer degradation plays a significant role in flame retardant action. It is on such processes that this chapter is focussed.

Some polymers can be said to be inherently flame retarded. Bourbigot and Duquesne [60] classified such polymers as having a continuous operating temperature range from 180°C to 300°C or above together with a decomposition temperature above 350°C. Such polymers can have high thermal stability due to their high aromatic content,e.g. polyarylates and polycarbonates, phenolic resins, aromatic polyesters, polyethers and polyamides, because they decompose to evolve flame inhibitors such as HCl from PVC, or contain blanket out any flames at high temperature. Poly(acrylo ketones) ether ketones have above average thermal and thermo-oxidative stability at high temperature which will result in resistance to fire.

Few polymers are inherently resistant to heat and fire. The traditional method of rendering them fire retarded is to include a flame retarded additive in the formulation during polymer processing. The choice of fire retardant depends on whether the fire retardant is required to predominately function in the gas phase, e.g. ATH, MgOH, halogen/ATO systems or the condensed phase via char formation enhancement, e.g. APP. In addition, the chosen additive must be stable at the polymer processing temperature whilst being compatible with the polymer itself. In addition, cost is another significant factor, e.g. ATH-containing plastic sheathing used as insulation for low cost electrical wiring. Gas phase retardants function by releasing species which either blanket out the flames with non-combustible gases such as water from ATH or halogen flame inhibitors from the halogen/ATO type systems. The incorporation of additives however does have several disadvantages. The additive is often required in high loadings to be effective (typically 10-40 wt %) which may result in adverse changes to the physical and mechanical properties of the polymer rendering the polymer unsuitable for a particular end-use. The alterative reactive fire retardant approach is to incorporate the fire retardant species, via copolymerisation or some other chemical modification, to produce what is essentially an inherently fire retarded polymer [61]. The relatively low load required to achieve sufficient fire retardance, and careful selection of the comonomer, can keep detrimental changes to the physical and mechanical properties at an acceptable level. Also, because it is chemically incorporated into the polymer, the fire retardant will not be easily loss from the polymer. Thus one of the major problems associated with additive systems is eliminated.

Because of the advantages and despite their higher costs, in recent years there has been a growing interest in the reactive approach to produce high value, high

performance fire retarded polymers. Because of the environmental pressures to reduce /eliminate the use of halogen–containing systems, much interest has focussed on phosphorus as the fire retardant moiety incorporated in the polymer chain. One example is the work of Price, Ebdon et al who have synthesised [62] and studied the flammability and decomposition behaviour [63, 64, 65] of poly(methyl methacrylate) and polystyrene polymers copolymerised with a range of phosphorus containing copolymers. Typical copolymers were diethyl(acryloyloxymethyl)phosphonate (DEAMP), diethyl(methacryloyloxymethyl)phosphonate (DEMMP), diethyl(acryloyloxyethyl)phosphate (DEAEP) and diethyl(methacryloyloxyethyl)phosphate(DEMEP). Their structures are given in figure 3.

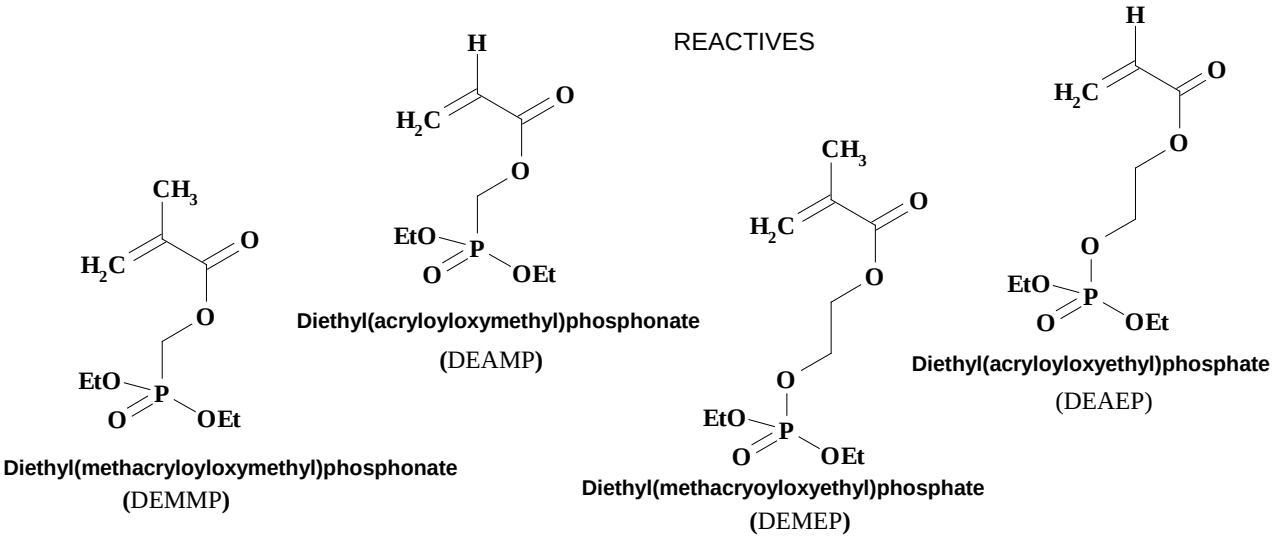


Figure 5. Structures of copolymers used for reactive fire retardant studies of Price, Ebdon et al [63, 64, 65]

The fire retardant mechanisms identified for the various phosphorus moieties in these PMMA and polystyrene copolymers investigated can be summarised:

- vapour phase fire retardant action assumed for gas phase phosphorus species released from all polymers
- the rate of volatile production was reduced for phosphorus-containing copolymers as compared to that of the corresponding additive system [65]
- the normal unzipping mechanism of PMMA decomposition was obstructed in the case of the acrylate copolymers thus reducing the evolution of the flammable MMA monomer
- condensed phase cross-linking occurred as the copolymer containing phosphorus decomposed facilitating char formation and reducing flammable volatile evolution

- Interference with the H-transfer reactions occurred during polystyrene decomposition for acrylate copolymers

7. Relevance of polymer stabilisation to flame retardance mechanism

It might be assumed that since condensed phase flame retardants function by modifying the normal thermal degradation mechanisms of polymers, that they would also function as thermal stabilisers and that thermal antioxidant stabilisers would show flame retardant properties. However, these statements are rarely the case and to understand why, it is necessary to compare the mechanistic aspects of flame retardance as discussed above with those of thermal degradation and thermal oxidation also briefly alluded to above and in the case of the latter, the Bolland and Gee mechanism [5] in Scheme 1.

Cursory comparison of the character and behaviour of flame retardants and thermal stabilisers including antioxidants yields the following:

- flame retardants are generally present at concentrations of greater than 10 wt% for them to be effective and relate to effective elemental concentrations in the case of phosphorus of the order of 2-4 wt% and in the case of bromine 5-10 wt% with respect to the polymer;
- thermal and photo-antioxidants are often present and effective at concentrations of the order of 0.5-1.0 wt%;
- flame retardants at low concentrations(≤1 wt%) are seldom, if ever, known to function as thermal stabilisers; and
- antioxidants when introduced at high concentrations (which would be very expensive given their relatively high costs), are not reported to be flame retardant.

There is only perhaps one significant case where low concentrations of an antioxidant shows flame retardant behaviour and that is in the case a certain hindered amine stabilisers (HAS) that at the normally used concentrations (≤1 wt%) offer low levels of flame retardancy in polypropylene and show synergy with bromine-containing flame retardants [66, 67, 68]. .

Before returning to this example, it is pertinent to review the mechanisms by which thermal antioxidant stabilisers work. Since thermal stability is determined inherently by the lability of bonds present within a polymer, the only means of offering thermal stabilisation is to offer means of scavenging or rendering inert impurities present which might sensitise degradation. So, for example, in PVC where release of hydrogen chloride sensitises further degradation, the presence of a basic additive such as metal carboxylates and even calcium carbonate has thermal stabilising properties. Similarly, the presence of radical scavengers such as hindered phenols, may interact and terminate impurity-generated radicals which might otherwise promote eventual chain scission mechanisms as shown in Scheme I.

Most thermal stabilisers fall into one of two groups, they function either as antioxidants or in some other manner such as buffers to remove excess acidity as exemplified by the PVC example above. In the case of antioxidants, these are often characterised according to their means of operation [3, 69, 70, 71]:

1. "Primary" antioxidants, also termed chain-breaking antioxidants, interfere with the chain reaction in Scheme I by trapping radicals or labile hydrogen atom donors. These are exemplified by hindered phenols and alkylarylamines. Scheme II schematically demonstrates the scavenging activity of a typical hindered phenol.
2. "Secondary" antioxidants or hydroperoxide decomposers (see Scheme 1) are typified by organosulphur species having reducing properties such as sulphides and thioethers. Tertiary phosphites also fall into this category (see SchemeIII).
3. Photoantioxidants are typified by the class of hindered light stabilisers (HAS) which although they were developed for photostabilisation of polyolefins, they also possess thermal antioxidant properties. They are generally assumed to function as "primary" antioxidants in that they scavenge radicals and in particular, peroxy radicals.
4. Metal ions and particularly heavy metal ions tend to sensitise peroxy radical formation and so the presence of metal scavenging or chelating species can offset this effect. This form of stabilisation is particularly important for polymers in which metal-containing polymerisation catalyst residues are present such as polyolefins. While simple additives like calcium stearate may be used, more sophisticated ones based on bifunctional chelating species also are available commercially.
5. Some redox systems have been developed for certain polymers. The copper/iodine system is well-established for polyamide thermal stabilisation and in spite of introducing a heavy metal ion into the polymer, works well in an oxygen-free environment [71].

Very often, antioxidants are used in combinations to ensure maximum activity and typically a commercial additive system may comprise both a primary and secondary antioxidant species, although total concentrations remain ≤1 wt%. Scheme IV shows schematically how a combination of primary and secondary antioxidants functions in a polyolefin matrix [70]. Some metal chelate scavengers may also be based on a tertiary phenolic structure thereby introducing two antioxidant properties into the same molecule.

Scheme II: Stabilizing activity of chain-breaking, primary antioxidants

$$R^{\bullet} + R'.OH \rightarrow RH + R'.O^{\bullet}$$

where R'.OH is a tertiary phenol, for example octadecyl 3,5-di(tert)-butyl-4-hydroxyhydrocinnamate) or Irganox 1076, Ciba (see Table 6); $R'.O^{\bullet}$ is a stable radical.

Scheme III: Stabilizing activity of hydroperoxide-decomposing secondary antioxidants

$R.OOH + (R'.O)_3.P \rightarrow ROH + (R'.O)_3.P = O$

e.g. where $R'.PO_3$ is an organophosphite, for example tris(2,4-di-tert-butylphenyl) phosphite or Irgafos 168, Ciba (see Table 6)

Scheme IV: Combined stabilizing activity of primary and secondary antioxidants [70].

Scheme IV

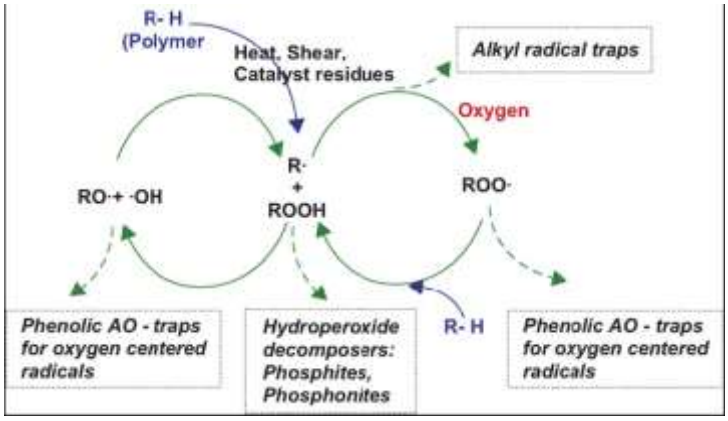


Table 6: Examples of primary, secondary and hindered amine antioxidants marketed by Ciba for use with polypropylene

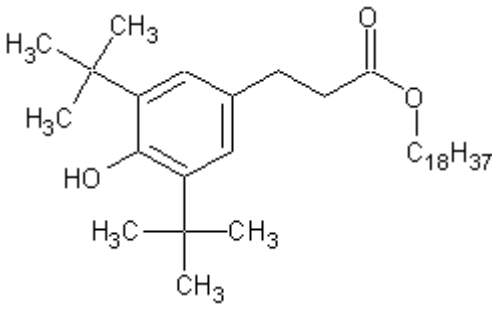
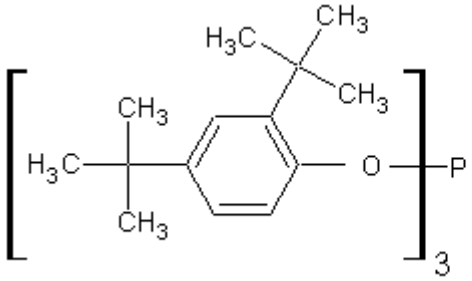
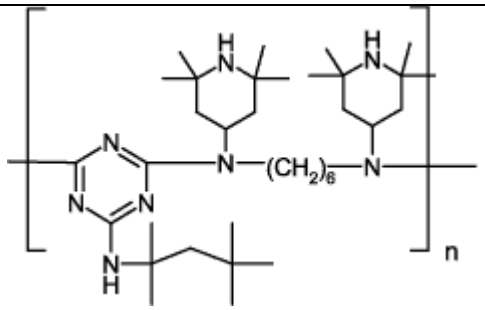
Type	**Commercial name (Ciba)**	**Chemical formula**
Primary (radical scavenger)	Irganox 1076	Octadecyl 3,5-di(tert)-butyl-4-hydroxyhydrocinnamate) 
Secondary (hydroperoxide decomposer)	Irgafos 168	Tris(2,4-di-tert-butylphenyl)phosphite 
Hindered amine stabiliser (combined light and heat)	Chimassorb 944	
Hindered amine stabiliser with flame retardant properties	Flamstab NOR116	The reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl) butylamino]- 6-chloro-s-triazine with N,N′-bis(3-aminopropyl)ethylenediamine) [CAS Reg. No. 191680-81-6]

Table 6 provides typical examples of each of these antioxidants from which it may be seen that they bear little resemblance to the flame retardant molecular structures described in the remaining parts of this book. However, notwithstanding this observation, it was briefly mentioned above that a recently developed HAS-based

system, commercialised as NOR116 by Ciba, is marketed as both a photoantioxidant and a flame retardant for polypropylene [arh ?]. While very little, if any, literature is available to explain its flame retardant activity, it is noteworthy that research into the burning behaviour by Stuetz et al [72, 73] 30 years ago suggested that the burning mechanism of polypropylene involves an oxidative pyrolytic step as a pre-requisite for fuel formation and so it is possible that the introduction of a HAS photoantioxidant will interfere with this stage thus promoting a flame retardant effect. That there is also synergy observed between NOR116 and bromine-containing flame retardants like decabromodiphenyl ether [74], for example, in which bromine radical formation and reaction determine flame retardant behaviour. It is possible that the radical interacting character of the HAS may have a beneficial effect on the effectiveness of the $Br^{\cdot}$ radicals in terminating flame chemical chain reactions.

8. Alternative polymer degradation processes, e.g. photochemical, plasma, irradiation and their potential influence on flame retardant behaviour.

In the previous section, comparison was made between the nature and means of operation of antioxidants (including some photoantioxidants), which are introduced into polymers to improve either processing or long term stability, and flame retardants, which may interact with and modify the thermal degradation process as well as the ensuing flame chemistry. It is evident that while there are considerable differences between the chemistries of flame retardancy and thermal (and photo-) stabilisation, there are similarities in that the polymer degradation pathways, while being specific for each polymer, are driven by thermal energy and involve the same thermal degradation pathways. A major difference is, of course, the rate of heating, which during normal polymer processing and long term exposures during service are generally low while in a fire are large. The effect of rate of heating was noted for the acrylic copolymers above where low rates favour carbonisation (and char-forming) whereas high rates favour volatilisation [26].

Since most polymer degradation processes tend to lead to chain scission, cross-linking or both, it might be assumed that flammability would be influenced by the degradation history of any given polymer. Cursory analysis of the literature shows that little if anything has been published on the effects of ageing or degradation on resulting polymer flammability. This is not to be confused with the loss of flame retardants during service life by leaching, cleaning or other process. Generally, however, the influence of polymer history of non-retarded polymers appears not to be an important issue since during the service life of a polymer, only a minority of polymer chains require to be broken before the polymer becomes unserviceable in terms of reduced tensile, impact or other significant property. In fact, most degradation processes comprising external agencies involve attack of polymer chains in the amorphous regions in the first instance. In highly crystalline polymers like polyethylene, polypropylene and aliphatic polyamides, for example, these comprise less than 50 wt% of the total polymer and often much less and so the majority of the polymer molecules present are non-degraded even when the overall polymer serviceability has reduced. Furthermore, it is generally noted during the weathering of linear crystalline polymers where the degrading agencies are a complex combination

of heat, light, water and possibly air polluting species, that crystallinity increases following internal relaxation of polymer chains after scission reactions have occurred. For example, weathering of linear low density polyethylene increases its degree of crystallinity from just less than 40% to over 55% during a 12 month period [75]. In other even more highly crystalline polymers like polypropylene (>70%), this means that nominally degraded polymer actually comprises a higher proportion of pure polymer in the crystalline phase with products of degradation concentrated in the minor amorphous phase. The effects of this concentrated but minor zone of degradation appear to have little effect on the overall flammability although research in this area would be welcome. This would be especially relevant to the generally amorphous polymers such as the thermosets, polystyrene and copolymers like EVA and ABS.

Conversely, degrading treatments that may modify a polymer surface in a manner that enables a subsequent or simultaneous modification to be undertaken may reduce polymer flammability. Such modifications could be seen to be potential flame retardant processes. Surface graft copolymerisation of an activated underlying polymer surface comes to mind here where activation during surface chemical grafting [76], radiation [77], preirradiation [78 79] and plasma [80] treatments are examples. This area may be considered to be an important and emerging means of conferring flame retardancy in a more sophisticated and both environmentally- and cost-effective manner than the traditional use of bulk flame retardants for a number of polymers. The current state of developments here along with the recent interest in depositing nanoparticulates on to polymer surfaces with a view to improving overall flame retardancy needs also to be mentioned and have been recently reviewed by ourselves with an emphasis on textile substrates [81].

Abbreviations;

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