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Flame Retardants

Polymer Blends, Composites and Nanocomposites

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Preface

The book on "Flame Retardants: Polymer Blends, Composites and Nanocomposites" summarizes many of the recent research accomplishments in the area of flame retardant such as state-of-art polyoxymethylene, flame retardancy of polymer nanocomposite, recent developments in different techniques used for the flame retardancy, recent development of phosphorus flame retardants in thermoplastic blends and nanocomposites, non-halogen flame retardants in epoxy-based composites and nanocomposites, flame retardant/resistant-based nanocomposites in textile, flame retardants in bitumens and nanocomposites, fire retardant for phase change material, flame retardant finishing for textiles, flame retardant of cellulosic materials and their composites. As the title indicates, the book emphasizes the various aspects of flame retardants and their nanocomposites. This book is intended to serve as a "one stop" reference resource for important research accomplishments in the area of flame retardant-based nanocomposites book. This book will be a very valuable reference source for university and college faculties, professionals, postdoctoral research fellows, senior graduate students, researchers from R&D laboratories working in the area of flame retardant-based nanocomposites. The various chapters in this book are contributed by prominent researchers from industry, academia and government/private research laboratories across the globe. It covers an up-to-date record on the major findings and observations in the field of flame retardant-based nanocomposites.

The first chapter on flame retardant-based nanocomposites gives an overview of the area of state of art, new challenges and opportunities of flame retardant-based studies and research. The following chapter provides good structure of flame retardancy of polymer nanocomposite. This chapter explained with many sub topics such as nanocomposite-based fire retardants, fire-retardancy mechanism of carbon-based nanocomposites, fire-retardant mechanism for clay-based nanocomposites, polymer nanocomposites combined with conventional fire retardants, nanocomposites combined with halogenated flame retardants, nanocomposites combined with phosphorus and intumescents, nanocomposites combined with metal hydroxides, other combinations, fire-protective coatings, intumescent coating, nanocoating. The next chapter mainly concentrates on developments in different techniques used for flame retardancy. The authors of this chapter discuss different types of instruments used for flame retardant nanocomposites; in the first half of this chapter the authors explained the main instruments such as cone calorimetry, UL94 and condensed phase pyrolysis and their usage, test principle, test specimens, test procedure, test report, etc. In the second half of this chapter is discussed polymer combustion smoke formation. Finally, the chapter discusses the future trends of nanotechnology of flame retardant catalysis technique, ceramic/glass shield, vapour phase flame retardant, flame retardant synergy. The fourth chapter discusses the development of phosphorus flame retardants in thermoplastic blends and nanocomposites. This chapter discusses many interesting topics such as phosphorus flame retardants, commercial products, degradation of phosphorus flame retardants, applications of phosphorus flame retardants, properties of phosphorus flame retardants, effects of phosphorus flame retardants in environment, phosphorus flame retardants in thermoplastic blends and nanocomposites and future trends.

Another chapter deals with the review of non-halogen flame retardants in epoxy-based composites and nanocomposites: flame retardancy and rheological properties. The authors of this chapter explain using different subjects such as mechanism of flame retardant materials in epoxy-based composites, review of reactive phosphorus-based flame retardant epoxy resins system, DOPO-derivatives flame retardants system, phosphors containing flame retardants system, review of rheological and mechanical properties of advanced epoxy resins containing DOPO-derivatives and review of inorganic and metallic-based flame retardants in epoxy resins. Another chapter on flame retardant/resistant-based nanocomposites in textile, explained with different subjects such as flame retardant for plastic, flame retardancy of textile, strategies with nanocomposite principle and their fire properties for textiles. Authors of this chapter also explained with many sub topics such as mode of actions, halogen-containing flame retardants inorganic compounds, charring and intumescent systems, burning behaviour and fire hazards of textile, flammability testing of textiles, and flame retarding systems for textile. The seventh chapter discusses flame retardants in bitumens and nanocomposites; from this chapter we can see different topics related to bitumens and their uses in flame retardant studies such as conventional flame retardant modified bitumen, new types of environmental friendly flame retardants using bitumen, bitumen/flame retardant nanocomposites, and future trends. The authors discuss in the eighth chapter fire retardants for phase change material, type of fire retardant, experimental work conducted by other researchers, experimental work performed at the University of Auckland and materials for fire testing. The subsequent chapter on flame retardant finishing for textiles gives explanations with many sub-topics such as fabrication, mechanism of combustion, mechanism of flame retardancy, chemistry of flame retardant additives, flame retardants (FR) for textiles, flame retardant testing methods, environmentally sustainable flame retardants: novel approaches.

The final chapter on flame retardant cellulosic materials and their composites explains the physical and chemical structure of cellulosic materials, fire and flame retardancy finishing of cellulosic materials, fire and flame retardancy finishing of cellulosic materials, and their composites.

Finally, the editors would like to express their sincere gratitude to all the contributors of this book, who gave excellent support for the successful completion of this venture. We are grateful to them for the commitment and the sincerity they have shown towards their contribution to the book. Without their enthusiasm and support, compilation of the book would not have been possible. We would like to thank all the reviewers who have taken their valuable time to make critical comments on each chapter. We also thank the publisher Springer for recognizing the demand for such a book, and for realizing the increasing importance of the area of "Flame Retardants: Polymer Blends, Composites and Nanocomposites" and for starting such a new project, in which not many other publishers have put their hands.

P.M. Visakh

Contents

Editors' Biodata

P.M. Visakh M.Sc., M.Phil. submitted his Ph.D. thesis to Mahatma Gandhi University, Kottayam, kerala, India. He is working now at Tomsk Polytechnic University, Tomsk, Russia. He edited 10 books from Scrivener (Wiley) and Springer and more than 15 books are in press (from Wiley, Springer, Royal Society of Chemistry and Elsevier). He has been invited as a visiting researcher to Portugal (2013, 2014), Czech Republic (2012, 2013) Italy (2009, 2012), Argentina (2010) Sweden (2010, 2011, 2012), Switzerland (2010), Spain (2011, 2012), Slovenia (2011), France (2011), Belgium (2012) and Austria (2012) for his research work. He has visited 15 universities in Europe. He published 5 publications, 3 reviews and more than 15 book chapters. He has attended and presented more than 28 conferences, he has 100 citations and his h-index is 5. His research interests include: polymer nanocomposites, bio-nanocomposites, and rubber-based nanocomposites, fire retardant polymers and liquid crystalline polymers and silicon sensors. e-mail: visagam143@gmail.com

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Chapter 1
Advances in Flame Retardant of Different Types of Nanocomposites

State of Art New Challenges Opportunities

P.M. Visakh

Abstract The present chapter deals with a brief account on various types topics in flame retardant of polymer nanocomposites. This chapter discussed with different topics such as flame retardancy of polymer nanocomposite, recent developments in different techniques used for the flame retardancy, recent development of phosphorus flame retardants in thermoplastic blends and nanocomposites, non-halogen flame retardants in epoxy-based composites and nanocomposites, flame retardant/resistant based nanocomposites in textile, flame retardants in bitumens and nanocomposites, fire retardant for phase change material, flame retardant finishing for textiles, flame retardant of cellulosic materials and their composites.

1.1 Flame Retardancy of Polymer Nanocomposite

From the application view polymers are very flammable materials, for preventing this flammability, scientists need to improve polymer fire retardancies, and this is a major challenging. Developing the effective environmentally friendly flame retardants is challenging. Because of this materials are very hazardous; they are widely used owing to their effectiveness and low cost. Flame retardant nanocomposites with conventional fire retardants to develop more-efficient materials showing improved mechanical properties. There are numerous nanofiller/conventional-fire-retardant already prepared. From some of the work related to CNTs shows that improve the flammable properties of nanocomposites also improved the mechanical properties such as electrical, thermal properties. Nanofiller-based flame retardants show high flame-retardant efficiencies. Nanofiller can reduce the peak heat release rates (PHRRs) of polymers and thus reduce the speed at which

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flames spread throughout them. Some of the works revealed the flame-retardancy mechanism of CNTs [1–9], shows that CNTs are most well-established material, they are prepared their fire-retardancy mechanism and some of their disadvantages. CNT-containing nanocomposites absorb more radiation than polymers during fires; therefore, nanocomposite temperatures increase faster than polymer ones.

The nanotube-network layer emits radiation from the material surface and acts as a barrier against the decomposed gas supplied from the bulk polymer and against oxygen diffusing from the air into the material, which accelerates polymer decomposition. The nanotube-network layer must be smooth, crack-free, and opening-free so that it may act as an effective gas barrier. Barus et al. investigated the thermal properties of three types of CNTs and found that the dispersivity of the CNTs themselves affects the thermal degradation of nanocomposites. The CNT load is also important in determining fire retardancy, and in fact, the optimal CNT load reduces PHRR. Dittrich et al. showed that graphene were the most effective carbon-based fire retardants. Montmorillonite is the most commonly used clay because it is naturally ubiquitous, can be obtained at high purity and low cost, and exhibits very rich intercalation chemistry, meaning that it can be easily organically modified. The fire-retardancy mechanisms for clay- and carbon-based nanocomposites are almost identical. One fire-retardancy mechanism is the reduction in PHRR due to the formation of a protective surface barrier/insulation layer consisting of clay platelets accumulated with a small amount of carbonaceous char [10, 11]. The key factor determining clay- and carbon-based-nanocomposite flame retardancy is the formation of a surface network layer. The barrier/insulation effect depends on the external heat intensity.

The flame-retardancy effectiveness of clay-based nanocomposites depends on the kind of matrix [12–26]. IT of polymers such as PP, polyethylene (PE), PS, ethylene vinyl acetate (EVA), and PMMA usually decreases when nanofiller is added, because the clay itself is possibly catalytic. Most researchers have concluded that polymer/clay nanocomposites should at least exhibit PHRR reduction if nanomorphology is achieved through exfoliation and intercalation. The difference in nanomorphologies does not significantly affect polymer/clay nanocomposite flame retardancy. Nanocomposites can be obtained by organomodifying clays, and is easily achieved through melt-compounding. However, organomodified clay surfaces degrade at high temperatures, rendering organomodification problematic in melt-compounding and decreasing nanocomposite flame retardancy. Metal hydroxides are widely used in fire retardants because they are safe and inexpensive and because they reduce the amount of smoke produced in fires. However, high loads (>60 wt%) are mandatory to satisfy the V-0 classification, which is required for most fire retardants, and such high loads degrade mechanical properties, resulting in inflexible materials. The main purpose of combining nanofillers with metal hydroxides is to reduce the metal-hydroxide load without deteriorating flame retardancy. Recently reported that calcium carbonate ($CaCO_3$) nanoparticles could improve both thermal and thermo-oxidative stability [27]. Applying a flame-retardant coating is one of the most effective and economical methods of protecting substrates from fire damage. Polymer bubbling causes the nanofillers inside materials to migrate to the surface, where they then act as a barrier against heat and mass transport and can reduce the heat intensity during combustion. It is expected that nanofiller-based coatings more efficiently reduce material flammability than materials containing nanofillers.

1.2 Recent Developments in Different Techniques Used for the Flame Retardancy

The most common approach to improve the flame retardancy performance of materials is to add flame retardants, such as halogen-based agents, phosphorous-based compounds, metal hydroxides, intumescent agents, boron and nitrogen-based flame retardants, etc. [28]. Simultaneously, smoke suppressants are developed because the majority of human deaths during fire incidents are related to the inhalation of smoke and toxic combustion gases, with carbon monoxide being particularly significant. Some approaches that were adopted to tackle this problem include the use of fillers or additives, surface treatments, and chemical or physical modification. Cone calorimeter is a modern device used to study the fire behavior of small samples of various materials in condensed phase. It is widely used in the field of fire safety engineering [29]. The cone calorimeter test has been developed for material fire evaluations, computer modeling, design purposes, and development and research to help make real world fire predictions. The test performance uses the bench-scale system to measure fire characteristics associated with heat and smoke output. The measurements can be used directly by researchers or can be used as data input into correlation or mathematical models used to predict fire development. The cone calorimeter became the premier dynamic research tool based on the principle of oxygen consumption calorimetry. The UL 94 V test is widely used both in industry and academic research centers, and is intended to meet industrial requirements as well as to hierarchically classify the polymeric materials [30].

UL 94 flame rating groups materials into categories based on their flammability. UL94 covers two types of testing: vertical burn and horizontal burn. Vertical burn test includes Vertical Testing (V-0, V-1, V-2), Vertical Testing (5VA, 5VB) and Vertical Testing of Thin Materials (VTM-0, VTM-1, VTM-2). Specimens molded from the plastic material are oriented in either a horizontal or vertical position depending on the specifications of the relevant test method, and they are subjected to a defined flame ignition source for a specified period of time [31]. Pyrolysis of polymeric materials is a complex process involving simultaneous combinations of heat, energy and mass transfer and diffusion, fluid dynamics and degradation chemistry [32]. The study on polymer combustion and fire retardancy is a complex multidisciplinary topic, encompassing physical and chemical phenomena occurring in the gas and condensed phase. Thus, aspects involved are physical chemistry of flames and thermal degradation of polymers, respectively [33]. Combustion and flammability of polymeric materials are important topics of practical interest directly related to fire safety [34]. Polymer combustion is a complex process involving a multitude of steps and is best described in qualitative terms. In general, four major steps comprise polymer combustion: ignition, pyrolysis, combustion and feedback [35]. Depending on the flammability limit of the material, ignition is normally caused by the presence of an external heat source such as a flame or a spark or, if the temperature is high enough, occurs spontaneously.

The combustion of polymers involves a variety of processes (both physical and chemical) occurring in several phases. Thus, polymer melting and degradation, heat transfer in both solid and liquid phases and diffusion of the breakdown products through the degrading polymer into the gas phase accompany the various combustion reactions which occur. Polymers with aliphatic backbones, or those that is largely aliphatic and oxygenated, have a tendency toward low smoke generation, while polyenic polymers and those with pendant aromatic groups generally produce more smoke [36]. The relative distribution of pyrolysis products from an individual polymer is dependent on the pyrolysis temperature, the heating rate and the pyrolysis atmosphere. The amount of smoke generated in a nitrogen atmosphere passes through maxima with increasing temperature in several of the polyesters whereas from others the smoke increases steadily with temperature. The structure of a polymer influences both flammability and smoke formation [37].

1.3 Recent Development of Phosphorus Flame Retardants in Thermoplastic Blends and Nanocomposites

Use of thermoplastics and thermosetting polymers on a large scale for applications in buildings, transportation, electrical engineering and electronics, a large variety of flame retardant products have been developed over the past 40 years. Phosphorus-containing flame retardants cover a wide range of inorganic and organic compounds and include both reactive products which are chemically bound into the polymer material as well as additive products which are integrated into the material by physical mixing only. They have a broad range of applications, and a good fire safety performance. The most important phosphorus-containing flame retardants are phosphate esters, phosphonates and phosphinates. Phosphorus-based flame-retardants can be characterized by their chemical structure and how they are incorporated into the epoxy molding compounds. They are usually divided into two categories: (1) inorganic derivatives: for example, ammonium polyphosphate (APP) and red phosphorus; and (2) organic derivatives such as aromatic phosphates: for example, triphenyl phosphate; alkyl substituted triaryl phosphates such as cresyl diphenyl phosphate, isopropyl phenyldiphenyl phosphate, tert-butylphenyldiphenyl phosphate, tricresyl phosphate, trixylyl phosphate, and so on, and oligomeric phosphates such as resorcinol bis(dipheny1 phosphate) (RDP).

Organic phosphorus compounds can be reacted directly into the polymer chain. Investigations have reported success in introducing phosphorus-containing functional groups into the backbones of epoxy. One of the advantages of organic phosphorus is that its reaction product with ambient humidity tends to be non-corrosive phosphorus compounds. This is not always the case with inorganic phosphorus. Red phosphorus has been reported to be most efficient as a flame retardant in oxygen containing polymers such as polycarbonates, polyethylene terephatalate (PET), polyamide and phenolic resins. Red phosphorus has been used as a flame retardant in polymeric material for almost 30 years [38]. Flame retardancy takes place due to formation of phosphorus-oxygen bonds that reduces the ester linkages into cross linking aromatic structures with lesser volatility. In addition the red phosphorus creates a heat shield on the polymer surface that results in flame retardant properties. Some drawbacks with the use of red phosphorus are the red color that could lead to discoloration of polymers and the formation of toxic phosphine gas during combustion and long term storage. Phosphorus flame retardants are widely used as adhesives and sealants, for building and construction, as lubricating fluids and greases, in paints and coatings as well as in thermoplastic materials. Key applications of PFR are in EPDM (ethylene propylene diene monomer) rubbers, PVC products, polystyrene, polyurethane foam, epoxy and phenolic resins.

Phosphorus-containing flame retardants (PFRs) have been used as effective flame retardants; the range of PFRs is extremely wide and diverse, since the element exists in several oxidation states. PFRs are widely used in standard and engineering plastics, polyurethane foams, thermosets, coatings, and textiles [39, 40]. Phosphate esters are mainly used as flame retardant plasticizers in polyvinylchloride (PVC, alkyl/aryl phosphates) and engineering plastics, particularly in polyphenylene oxide/high impact polystyrene (PPO/HIPS), polycarbonate/acrylonitrile butadiene styrene (PC/ABS) blends and polycarbonate (PC, e.g. triphenylphosphate, resocinol- and bisphenol A-bis-(diphenyl) phosphate). Many of the of phosphorus flame retardants are additives, and not chemically bonded to the final products, which may result in an easy release to the environment from furniture, electronic equipment, carpets, and also into the atmosphere from different sources such as buildings and vehicles [41].

The red phosphorus-based flame-retardant was coated with a primary coat of aluminum hydroxide and a secondary coat of phenol resin. The content of red phosphorus in the coated flame-retardant is preferably 60–95 % by weight. When the red phosphorus content is less than 60 % by weight, it becomes necessary to incorporate a large amount of the flame-retardant into the epoxy resin composition and the addition of a large amount of the flame-retardant decreases the moisture resistance of the encapsulant. When the content of red phosphorus exceeds 95 % by weight based on the weight of the flame-retardant, there is a problem in respect to the stability of the red phosphorus.

1.4 Non-halogen Flame Retardants in Epoxy-Based Composites and Nanocomposites

Epoxy resins are one of well-known thermosetting polymers and used for coating and adhesive applications, which can also be reinforced with fibers or additives for obtaining high strengths and good chemical resistances [28, 42–44]. It is reported that almost 65 % of glass-fiber reinforced composites have been consumed at the sectors of transport and construction. However, they are intrinsically combustible and needed flame retarded. The majority of flame retardants for epoxy resins are currently halogen-based flame retardants because their flame retardancy is very effective at gas phase and cost-effective at an industrial scale. Tetrabromobisphenol A (TBBA) is the leading halogenated flame retardant in epoxy resins system for electrical and electronic devices since it has good thermal stability and flammability as well as high Tg when it is formulated with curing agents.

In epoxy resins formulation, phosphorus-containing flame retardants can be applied as an additive, which is relatively easy to manufacturing process. However, it has some technical drawbacks, such as particle dispersion and deterioration of the physical properties of epoxy laminates when its loading is too high [45]. Thus, molecularly reactive phosphorus-containing flame retardants have been used for advanced epoxy laminates, which can give better performance on flame retardancy and material properties.

Thus, a variety of phosphorus-based flame retardants have been developed and studied for their flammability as well as rheological and mechanical properties. Recently, the two review papers extensively focused on the flame retardancy of non-halogen flame retardants for epoxy resins system [46].

Several research groups have reported that organophosphates or organophosphine oxides can be chemically pre-reacted to epoxy resins, which also imparts good flame retardancy to the cured epoxy resins [47–52]. Cheng et al. reported that di-epoxide containing phenyl phosphate [V] could be cured with DDS having 29–31 in LOI. However, the cured epoxy resin had a lower thermal stability and higher % P content needed to obtain the better flame retardancy. Moreover, the high level of the % phosphorus content may be caused to lower the glass transition temperature (Tg) of the cured epoxy resins. Thus, the % P content in a finial epoxy formulation has to be reduced while other materials properties remain as same. Ren et al. showed that the phenyl phosphine oxide with bis-phenoxyl (VI) was synthesized with the epoxy resins and then cured with DDS in which 34 of LOI and good thermal stability (~357 °C at 5 % weight loss in N_2) were obtained.

DEGBA is a good cross-linked and relatively produces higher residues because of the bisphenol groups in its backbone. It can be also synthesized with a variety of phosphorus-based flame retardants. Lin et al. reported that the amount of % P was reduced by replacing the bis-phenoxyl with bis-diphenoxyl group in the

DEGBA epoxy resin, where only 1.5 % P could be contributed to achieving above 30 in LOI, high Tg (180 °C) and higher residues remained (26 % in N_2). In the report, the advanced epoxy resins with the phosphorus-based flame retardant [VII] had the highest number of LOI obtained among the epoxy resins with other flame retardants, such as TBBA, DHBP (dihydroxybiphenyl) and PPA (phenyl phosphonic acid).

The mobility of an entangled polymer chain is frequently determined by a glass transition temperature, which is an indication of a relaxation statue of the entangled polymer chains. Unlike thermoplastic polymers, epoxy monomers can be chemically cross-liked at elevated temperatures by either itself or the aid of curing agents. Thus, a Tg of a cured epoxy resins can depend on the type of epoxy resins, curing agents and curing temperatures as well as flame retardants. It is important for epoxy laminates to obtain higher Tg at a low level of % P content, which may be a key factor to prevent a failure of the PCT (pressure cooker test) or soldering bath at electronic applications.

1.5 Flame Retardant/Resistant Based Nanocomposites in Textile

The nanomaterials strategy is one of several principles for improving the burning behavior of textiles. Textile requires effective flame retardancy properties with a minimal environmental impact, since these structures are often washed and flame retardant additives of coating can leach out into the environment [53, 54]. Flame retardant additives may have a mode of action in gas phase to extinguish the flame by radical inhibition or dilution, that leading to the decrease of the flame temperature or to reduce the availability of flammable gases and oxygen; and/or in condensed phase, in the vicinity of the flame to perturb the thermal degradation of the substrate by dehydration and char formation. Flame-retardant materials are a major business for the chemical industry and can be found practically everywhere in modern society. However, many additives have detrimental effects on the environment and human health and thus should be limited in use.

The fire behavior of a fabric largely depends on the chemical nature of the fibers that compose it. Also the same major flame retardant products for polymeric materials in general are found in textiles. Furthermore, the quantities of smoke released by fabrics from fiber blends are very difficult to predict. Indeed both polyester/wool and polyester/cotton blends release a much greater amount of smoke than the fibers alone. Finally, the presence of fire retardant in a material usually leads to a larger amount of smoke either by inhibition of the oxidation reaction generating incomplete combustion (fire retardant agent acting in the gas phase such as those based on halogen) or by reduction of the heat flux that the flaming combustion turns at time into smoldering.

1.6 Flame Retardants in Bitumens and Nanocomposites

Much attention has been paid to halogen-free flame retardants in the past two decades [55, 56]. Based on the exits problems of conventional flame retardants modified bitumen, it is of much significance to develop new types of environmentally friendly flame retardant bitumen. Some new environmental friendly flame retardants bitumen has been developed at present, such as inorganic hydroxide flame retardant bitumen, intumescent flame retardant bitumen, nanometer flame retardant bitumen and so on. Combustion processes of bitumen and bitumen/magnesium hydroxide composite are both multistage, and the volatiles are different in each temperature interval. After adding MH into bitumen, the temperature rise of bitumen matrix is inhibited due to magnesium hydroxide thermal decomposition.

Now a kind of environmental friendly flame retardant, intumescent flame retardant (IFR) is developing at a rapid pace, whose main active components are phosphorus and nitrogen. It is halogen-free, efficient and smoke-suppressive flame retardant. IFR is mainly composed of acid source, carbon source and air source, which respectively act as dehydrant, carbonific and foamer. Generally, the acid source, carbon source and air source of IFR respectively are ammonium polyphosphate (APP), pentaerythritol (PE) and melamine (MA) [57–60]. Nanocomposite technology is the newest class of flame retardant materials. As tiny particle size, nanometer has many excellent performances such as tiny size effect, surface effect, and macroscopic quantum tunnel effect.

1.7 Fire Retardant for Phase Change Material

Phase change materials (PCM) are used in a wide range of applications including latent heat thermal energy storage in buildings [61]. One of the most suited PCM are paraffin, fatty acids and their esters because it has many desirable properties such as high latent heat of fusion, varied phase change temperature, negligible super cooling, and lower vapour pressure in the melt, chemically inert and stable, self-nucleating, no phase segregation and commercially available at acceptable cost. The first type, and the most common, is known as flame quencher. Halogenated alkanes have the ability to limit or extinguish nearby flame source. In the presents of fire, oxide and hydroxide free radical are formed and reacts to fuels the propagation of fire. When halogenated alkanes are present, they react with oxide and hydroxide free radical to give an inactive halogen free radical. Halogen free radical is less reactive than oxide and hydroxide radical therefore its presence retards the spread of fire [62].

The second type is called heat absorber. Materials such as magnesium hydroxide and aluminium hydroxide, which absorb heat from the surrounding and decompose endothermically preventing nearby material from heating up and hence minimizing its combustion. The last type is known as synergist, and is of two types, one which is not a fire retardant but can work with other types of fire retardants to improve their fire retardancy. Antimony oxide is known as a synergist for halogenated alkanes. The second type (will be refer as synergist system) is where two or more fire retardants work together to improve overall fire retardancy of a material. Montmorillonite clay (MMT) can be used as a synergist for intumescent fire retardant and heat absorber [63, 64]. MMT has two opposing effects on the composite. One is barrier effect, MMT works by forming carbonaceous-silicate charred layer at the surface which protects the underlying material from heating up. The other is catalytic effect towards the degradation of polymer matrix which decreases thermal stability. Aluminium hydroxide and magnesium hydroxide had little effect in improving fire retardancy of the composite. Addition of heat absorber reduced dripping but a very small residue was obtained after burning.

1.8 Flame Retardant Finishing for Textiles

Inorganic compounds are suitable for use as flame retardants in textiles, due to their decomposition temperatures in the range 150–400 °C. Unlike organic compounds, inorganic flame retardants do not evaporate under the influence of heat; rather they decompose, giving off non-flammable gases like water, carbon dioxide, sulphur dioxide, hydrogen chloride, mostly in endothermic reactions. Due to their properties to reduce the content of combustible products and to modify the thermal conductibility of the material, they are used alone or in combination with other flame retardants to obtain the required fire retardant properties. Aluminium trihydroxide (Al(OH)3): is the most widely used flameretardant. It is inert mineral filler, a non-toxic, white, crystalline powder and is included in the inorganic flame retardants. At about 250 °C, this compound is decomposed to form aluminium oxide and water, thus obtaining a non-flammable protection on the surface of the treated material. The most important commercial flame retardants can be classified into three categories: flame retardants based on phosphorus (condensed phase mechanism) and halogens (gas phase mechanism), synergistic systems containing flame retardant enhancers (nitrogen-phosphorus and antimony-halogens) and flame retardants with physical effects (alumina, borate). Some of these treatments have serious drawbacks: for instance the use of halogens as flame retardants is restricted because of the toxicity of their combustion gases, whereas although inorganic salts can provide excellent flame retardant properties for cellulose, they have very poor laundering durability. Polyester fibers are very easily ignitable, especially when they are blended with cotton fibers. It burns strongly and may drip, carrying flames to other surfaces. In fact, the molten material can form drops act as a second source of ignition and cause more rapid development of the fire.

1.9 Flame Retardant of Cellulosic Materials and Their Composites

Cellulosic fabrics have low fire resistance. They are composed of carbon and hydrogen (fuels) and oxygen (supporter or combustion) and burn very easily. The burning process of cellulosic materials is an oxidation process. This process may be accompanied by a flame or glow; most organic fibres undergo a glowing action after the flame has been extinguished. The glow may cause much damage as the flaming itself, since it can completely consume a textile. Flaming and glowing are distinctly different processes, taking place at different temperatures. It is useful, however to define a number of terms before going into details of fire and flame retardant finishing of textile.

This term is applied to textiles, which are essentially unaffected fire. This means that they do not support fire (flame or glow) and that there is little or no chemical or physical change when the textile is exposed to flames. Few textiles fall in this category. Carbon, asbestos, basalt and glass fibres are the one in common use today [65–67].

In the development of better flame retardants it is helpful to know what chemical reaction occur when cellulose burns and how the reaction are affected when fabrics are treated with a flame retardant. The burning characteristics of cellulose depend to a considerable extent on the chemical and thermal properties of the anhydroglucose units, on the availability of oxygen, and on the nature of noncellulosic materials that may also be present. Fibre properties such as the ignition temperature, the rate and heat of combustion products, and moisture content also affect the burning characteristic of cellulose [68, 69]. Ignition is controlled by various factors such as heat transfer from the source of ignition to cotton, thermal decomposition of cotton and reactions of decomposition products with the environmental oxygen. Thermal decomposition of cotton release a large number of combustible gases which can sustain ignition at and above certain concentration levels with oxygen of the air. A burning fabric generating more heat requires less ignition energy to continue its burning.

Most commercial treatments for cellulose are based on phosphorus, and consequently the effect of the structure of phosphorus based materials on the mechanism and efficiency of flame retardancy has been widely studied. Acidic phosphates act via phosphorylation, presumably at the C-6 hydroxyl of the anhydroglucose unit [70]. Consequently, increases of esterification are likely to be more efficient in promoting flame retardancy.

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Chapter 2
Flame Retardancy of Polymer Nanocomposite

Yoshihiko Arao

Abstract Nanofillers such as carbon nanotubes and clay are attractive materials, because addition of small amount of nanofillers can improve mechanical, thermal and electrical properties of plastics without changing processability. However, nanofillers themselves do not show excellent fire retardancy such as self-extinguish properties. Nanofillers should be combined with other fire retardants. Some combination showed positive synergy effect in fire retardancy, but some case showed negative synergy. It is important to know fire retardant mechanism of nanofiller to develop more efficient fire-retardant nanocomposites. In this chapter, we'll show the fire retardant mechanism of nanofillers. Then, effective combination of nanofiller and conventional fire retardant is introduced reviewing lots of papers.

2.1 Introduction

The use of polymers is increasing every year. The average annual increase in plastic use from 1950 to 2009 was ~9 % [1] because of their remarkable combination of properties, low weights, and ease of processing. However, plastics are highly flammable increasing their risk as fire hazards when used in practical applications. Consequently, improving polymer fire retardancies is a major challenge for extending polymer use to most applications.

The development of fire retardants is subject to regulations. Halogen-free, recyclable, environmentally friendly flame-retardant systems that do not release toxic gases have recently become preferable. For example, the waste electrical and electronic equipment (WEEE) and restriction of hazardous substances (RoHS) directives limit the use of bromine-based flame retardants. Polybrominated biphenyl

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(PBB) and polybrominated diphenyl ether (PBDE) were prohibited because, like dioxin, they are toxic to humans. Developing effective environmentally friendly flame retardants is challenging. Although bromine-based fire retardants have previously been recognized as hazardous, they are widely used owing to their effectiveness and low cost. However, bromine-based fire retardants are gradually being phased out owing to the WEEE and RoHS regulations.

It is expected to develop safe, eco-friendly fire retarded polymer nanocomposite to replace halogenated flame retardants. Nanocomposite research has progressed owing to contributions of numerous researchers, and the fire retardancy mechanisms of various nanocomposites are revealed. However, nanofillers themselves do not show excellent fire retardancy such as self-extinguish properties. Nanofillers should be combined with other fire retardants. There are infinitely many combinations of fire retardants, some of which may counteract the fire retardancy mechanisms. It is important to understand the fire retardancy mechanism of each material and choose effective combinations.

There are several excellent review papers on polymer fire retardancy. Morgan et al. show various applications and future trends for the fire retardancy of polymers [2]. Laoutid et al. and Dasari et al. summarized a vast amount of research on the fire retardancies of fundamental polymers and polymer nanocomposites [3, 4]. Morgan reviewed the flame retardancy of layered silicate nanocomposites, focusing on the effects of combining conventional polymers with nanofillers developed to 2006 [5]. A significant amount of research on combining flame retardant nanocomposites with conventional fire retardants to develop more-efficient materials showing improved mechanical properties has recently been reported. There are numerous nanofiller/conventional-fire-retardant combinations, so they should be summarized. In addition, some new technologies have been developed to improve flame retardancy. Thus, this chapter will show the flame retardancy mechanisms, especially those for nanocomposite/conventional-nanofiller combinations. Nanocoating technology (which is a versatile, cost-effective tool for improving flame retardancy) will also be introduced.

2.2 Nanocomposite-Based Fire Retardants

Polymer nanocomposites have recently attracted extensive attention in materials science because they often exhibit properties quite different from those of their counterpart polymer microcomposites whose matrices contain the same inorganic components. The surface areas of nanofillers are drastically increased so that polymer nanocomposites show macro/micro/nanointerfaces. Adding (CNTs) can improve not only the mechanical properties but also the functionalities such as electrical, thermal, and flammable properties of composites.

CNTs are one of the most typical nanomaterials used to give unique properties to polymers. Technology for the large-scale production of CNTs has recently been developed, decreasing the price of CNTs to ~$100/kg in 2013. Consequently, some

CNT-based nanocomposites have started appearing. For example, Evonik Industries is producing molding PA12 CNT-containing compounds for fuel lines [6]. The main advantage of this material is that it can avoid ignition induced by electrostatic charges. Fire risk can be substantially reduced by producing percolation networks of CNTs in polymers. Adding CNTs to polymers also modifies their flammabilities.

Nanofiller-based flame retardants show high flame-retardant efficiencies. Adding only a small amount (i.e., <5 %) of nanofiller can reduce the peak heat release rates (PHRRs) of polymers and thus reduce the speed at which flames spread throughout them. Further, the small amount of nanofiller does not reduce polymer processability and can improve the mechanical properties of polymers. However, adding only nanofiller cannot produce self-extinguishing (V-0, −1, and −2) polymers, which are required for most fire retardant products. The nanofillers should be combined with other conventional flame retardants to give a better balance of flammability/mechanical properties. The effects of combining nanofillers and flame retardants will be presented in Sect. 2.3.1. Further, the technology used to produce reliable nanocomposites requires great care and skill because nanofillers are relatively new, the technology is not yet completely understood, and polymer nanocomposite structures are unique. Thus, Sect. 2.2 summarizes the flame-retardancy mechanisms of the typical nanofillers used in carbon- and clay-based nanocomposites.

2.2.1 Fire-Retardancy Mechanism of Carbon-Based Nanocomposites

Nanocomposites can be classified into three categories according to the number of dimensions of the nanofillers (<100 nm) dispersed in polymers: (1) lamellar, (2) nanotubular, and (3) spherical polymer nanocomposites. Carbon-based nanomaterials showing such morphologies are thus named graphene, carbon nanotubes (CNTs), and carbon black (CB), respectively. Graphene is the completely exfoliated structure of graphite (single layer). The method of producing graphene was established recently, so graphene has attracted significant research interest [7–11]. CNTs are commonly used as fillers to improve the mechanical, electrical, and flame-retardancy properties of nanocomposites. Kashiwagi et al. revealed the flame-retardancy mechanism of CNTs [12–20]. Since CNTs are the most well-established material, we present mainly their fire-retardancy mechanism and some of their disadvantages here.

Figure 2.1 shows the cone-calorimetry results for single-wall nanotube and poly(methyl methacrylate) (PMMA) composites. Ignition time (IT), peak heat release rate (PHRR), and total heat release rate (THRR) are the important parameters in cone calorimetry to characterize material flammability. PHRR is the most important parameter used to describe flammability and is assumed as the driving force of the fire. Adding CNTs can reduce the PHRR; that is, the combustion heat intensity. However, it cannot change the THRR because CNTs do not act in the vapor

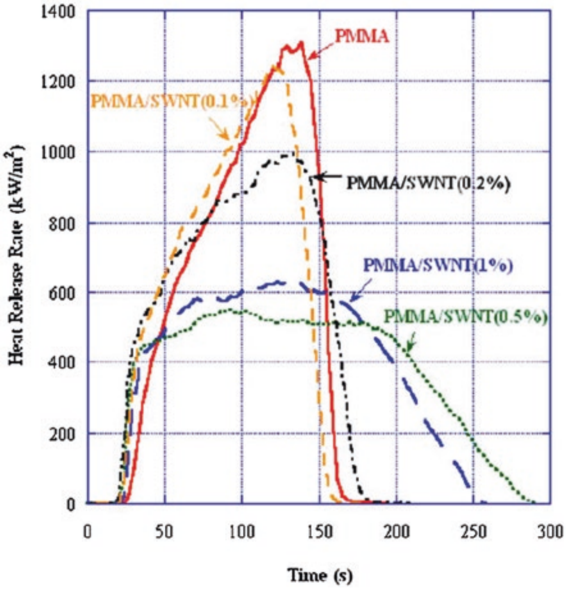


Fig. 2.1 Effects of SWNT concentration on mass loss rate of PMMA/AWNT in a nitrogen atmosphere (reprinted from [14])

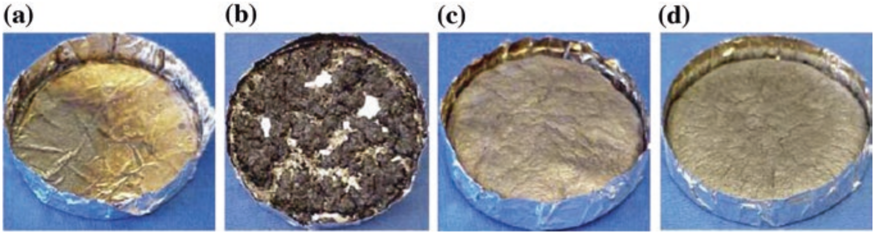
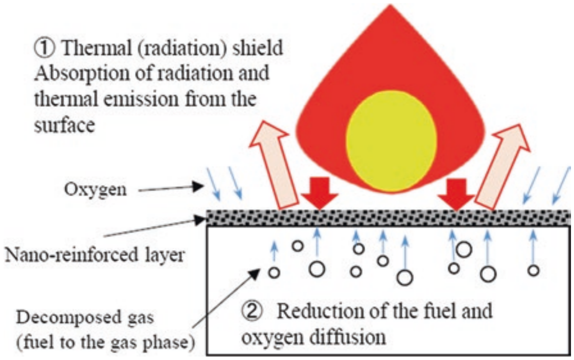


Fig. 2.2 Residues of PMMA/SWNT after the gasfication tests in a nitrogen atmosphere **a** PMMA, **b** PMMA/SWNT (0.2 %), **c** PMMA/SWNT (0.5 %), **d** PMMA/SWNT (1 %) (reprinted from [14])

phase, meaning that the amount of fuel gas required for combustion is not changed by adding CNTs. CNTs accelerate flame ignition (i.e., they reduce the IT). Most polymer/CNT composites show these tendencies. Kashiwagi et al. observed the residues (Fig. 2.2) after the cone calorimetry tests. The rate of PHRR reduction was small for the nanocomposite containing 0.2 wt% filler, as shown in Fig. 2.1. Many black discrete islands had formed during the test. In contrast, the surfaces of the nanocomposites containing >0.5 wt% CNTs were entirely covered with uniform, crack-free, opening-free CNT network layers, which significantly reduced the PHRRs. The key point of nanocomposite fire retardancy is the formation of a uniform CNT layer.

CNT-containing nanocomposites absorb more radiation than polymers during fires; therefore, nanocomposite temperatures increase faster than polymer ones. The ITs of materials decrease because the CNTs absorb large amounts

Fig. 2.3 Fire-retardant mechanism for nanoparticles



of radiation. Polymers begin to burn when they are heated to temperatures at which thermal degradation begins. The degradation products are superheated and nucleated to form bubbles. The bubbles burst at heated surfaces, evolving their contents as fuel vapor into the gas phase. There are a couple of possible mechanisms through which CNTs accumulate at material surfaces: the force of numerous rising bubbles during combustion pushes the CNTs to the material surface or the force of the polymer receding from the material surface during pyrolysis, leaving behind the CNTs.

The fire-retardancy mechanism of the CNT or char layer is depicted in Fig. 2.3. Kashiwagi et al. showed that close to 50 % of the incident flux was lost through emission from the hot nanotube surface layer and that the reminder of the flux was transferred to the nanotube-network layer and the virgin sample [14]. The nanotube-network layer emits radiation from the material surface and acts as a barrier against the decomposed gas supplied from the bulk polymer and against oxygen diffusing from the air into the material, which accelerates polymer decomposition. The nanotube-network layer must be smooth, crack-free, and opening-free so that it may act as an effective gas barrier [15]. Surface-layer cracks deteriorate nanocomposite flame retardancy during combustion.

Rheological properties appear to dominate the production of smooth CNT networks or char layers for all carbon-based nanocomposites [11, 15, 19]. Figure 2.4 shows rheological properties typical of PP/CB nanocomposites [19]. Neat PP shows typical low-frequency $G'-\omega$ scaling, where ω represents the oscillatory frequency. In contrast, the low-frequency G' scaling disappears, and G' becomes nearly constant at low frequency for the nanocomposites containing >5 wt% CB, meaning that the nanocomposite transitions from a liquid to a solid, which accompanies the formation of a mechanically stable network structure. It is well known that nanocomposites behaving like liquids cannot produce smooth CNT network layer on the material surface. The bubbles bursting at the surface disrupts the formation of an accumulation layer. Nanocomposites behaving like solids, on the other hand, contain bubbles that remain small in the high-viscosity layer and transport to the material surface, which tends not to disrupt the formation of the accumulation layer [14].

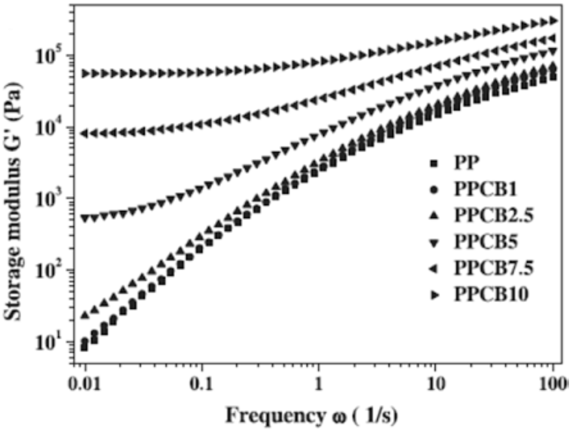


Fig. 2.4 The rheological properties of neat PP and PP/CB nanocomposites (reprinted from [19])

Uniformly dispersed nanocomposites show rheological properties similar to those of true solids. Therefore, the dispersion of carbon-based nanofillers determines the quality of the surface layer formed during combustion and thus affects the nanocomposite flame retardancy. Choosing appropriate CNTs is important. Barus et al. investigated the thermal properties of three types of CNTs and found that the dispersivity of the CNTs themselves affects the thermal degradation of nanocomposites [18]. The CNT load is also important in determining fire retardancy, and in fact, the optimal CNT load reduces PHRR, as shown in Fig. 2.1. Adding more CNTs once the uniform surface layer has formed deteriorates flame retardancy because it facilitates the agglomeration of CNTs and improves heat conductivity. The CNT aspect ratio affects fire retardancy, and higher aspect ratios lead to greater reductions in PHRR [16], indicating that a method of compounding thermoplastics to disperse CNTs and leave them longer is desirable.

From a practical perspective, a twin-screw extruder can be used to first compound thermoplastics, which are subsequently injection-molded in order develop a method of mass-producing thermoplastic-based goods. The relations between processing and flame-retardancy effectiveness should be discussed to apply CNTs in commercial products such as flame retardants. In fact, dispersing CNTs through a twin-screw extruder is worse than the nanocomposite produced using a closed kneader. Furthermore, injection molding orients material fibers. How these affect nanocomposite flammability should be discussed. Pötschke et al. investigated the relations between CNT dispersion and processing conditions [21–23]. They focused on the electrical conductivities of nanocomposites and conducted comprehensive experiments. Effective compounding methods are important for developing low-CNT-load fire-retardant nanocomposites.

Other carbon-based materials such as CB and graphene have also recently been investigated as flame retardants. Dittrich et al. showed that graphene were the most effective carbon-based fire retardants [11]. Interestingly, Wen et al. found new fire-retardancy mechanism for CB [19]. They showed that peroxy radicals, the chief factor affecting the thermal decomposition of polypropylene (PP), could be efficiently trapped in CB at elevated temperatures to form a gelled-ball crosslinked network. The PHRR was reduced 75 % and the LOI improved from 18 to 27.6 % by combining CB (to trap the peroxy radicals) and CNT (to create the networked layer) [20]. Surprisingly, adding CB and CNTs decreased the THRR; other nanocomposite systems do not show this tendency. The new fire-retardancy mechanism for CB has the potential to further improve the flame retardancy of carbon-based nanocomposites.

2.2.2 Fire-Retardant Mechanism for Clay-Based Nanocomposites

Montmorillonite is the most commonly used clay because it is naturally ubiquitous, can be obtained at high purity and low cost, and exhibits very rich intercalation chemistry, meaning that it can be easily organically modified. The natural clay surface is hydrophilic, so the clay easily disperses in aqueous solutions but not in polymers. Natural clays are often modified using organic cations such as alkylammonium and alkylphosphonium cations, forming hydrophobic organomodified clays that can be readily dispersed in polymers. Clay-based nanocomposites are usually classified into three categories because clay properties are unique: (1) immiscible (also known as microcomposites), (2) intercalated, and (3) exfoliated (also known as delaminated). Exfoliated nanocomposites are usually desired because they show improved mechanical properties [24]. Clay-based nanocomposite loaded with <5 % clay is already used as a commercial flame retardant because of its improved mechanical properties and flame retardancy [5].

The fire-retardancy mechanisms for clay- and carbon-based nanocomposites are almost identical. One fire-retardancy mechanism is the reduction in PHRR due to the formation of a protective surface barrier/insulation layer consisting of clay platelets accumulated with a small amount of carbonaceous char [25, 26]. The clay platelets accumulated because the clay remaining on the surface from polymer decomposition and clay migration was pushed by numerous rising bubbles of degradation products. The surface quality appears to determine the flame-retardant efficiency. Another mechanism suggested by Wilkie et al. is that the paramagnetic iron in the matrix traps radicals and thus enhances thermal stability. In fact, adding only 0.1 wt% iron-containing clay reduced the polystyrene (PS) PHRR by 60 % [27]. This effect was not observed for carbon-based nanocomposites because most of their iron is not on the surface and because their contact with the polymer is minimal [12].

Figure 2.5 shows HRR curves typical for polymer- and clay-based nanocomposites [25]. Adding clay can reduce the PHRR and generally reduces the IT, but it cannot vary the THRR. Carbon-based nanocomposites show the same tendencies because the fire-retardancy mechanisms for clay- and carbon-based nanocomposites; i.e., the barrier/insulation effect, are identical. Therefore, the key factor determining clay- and carbon-based-nanocomposite flame retardancy is the formation of a surface network layer. The barrier/insulation effect depends on the external heat intensity.

Fig. 2.5 HRR plots for pure PP, PP/C18, PP/Na-MMT, PP/H-MMT and PP/OMMT (reprinted from [25])

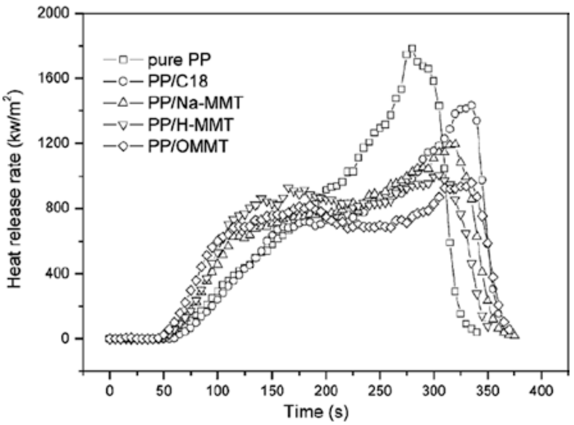
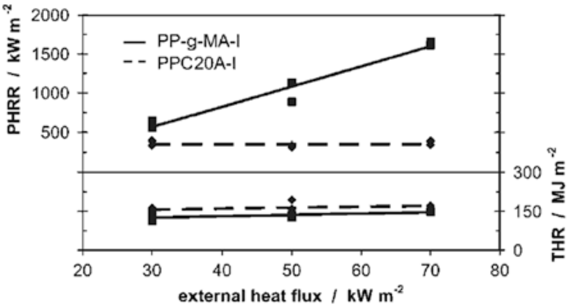


Fig. 2.6 PHRR and THR plotted against the external eat flux for PP (PP-g-MA-I) and nanocomposite (PPC20A-I) (reprinted from [28])



Schartel et al. investigated the relations between HRR and external heat flux, as shown in Fig. 2.6 [28]. THRR does not depend on external heat flux for the PP and nanocomposites. The PP PHRR, on the other hand, increases with increasing external heat flux, although the nanocomposite PHRR does not change. The fire-retardant efficiency strongly depends on irradiance such that the nanocomposite fire retardancy diminishes with decreasing irradiance. The results obtained through extrapolation to small irradiances correspond to flammability scenarios such as LOI and the UL 94 test. These results explain why adding nanofillers cannot drastically improve LOI and UL classification. In addition, they imply that adding nanofiller is effective for polymers exhibiting high HRRs.

The flame-retardancy effectiveness of clay-based nanocomposites depends on the kind of matrix [26–41]. For instance, the IT of polymers such as PP, polyethylene (PE), PS, ethylene vinyl acetate (EVA), and PMMA usually decreases when nanofiller is added, because the clay itself is possibly catalytic. In contrast, the IT of the PA6 nanocomposite increased when the nanoclay was added. Furthermore, rate at which PHRR decreases depends on which polymer matrix is used. PA6 and PS both decrease PHRR ~40–75 % [26, 32, 33, 37]. PMMA, on the other hand, only decreases PHRR 10–30 % [38–40]. Wilkie et al. showed that polymer nanocomposites such as PA6 and PS, which significantly reduce PHRR, exhibit significant intermolecular reactions and that the degradation pathway changes by incorporating nanoclay, whereas the PMMA did not show any change in the polymer degradation pathway or any significant HRR reduction [41]. Although adding the nanoclay to the PMMA does not significantly affect PMMA flammability, adding nanosilica to high-viscosity PMMA decreases PHRR by 50 % because silica covers the entire surface [42]. Incorporating nanoclay into PMMA is possibly effective when the nanoclay covers the entire PMMA surface. The nanoclay was less effective in improving PMMA fire retardancy possibly because the low viscosity of the PMMA prevented the nanoclay from covering the entire PMMA surface.

Modifying clay surfaces is the most important parameter for improving the fire retardancies of clay-based nanocomposites. Microcomposites are obtained instead of nanocomposites when unmodified clays are incorporated to polymers. The flammabilities of the microcomposites are usually almost identical to or sometimes worse than those of the pure polymers. Organomodifying clays produce intercalated or exfoliated nanocomposites. In addition, the char content and cone-calorimetry behavior of organomodified nanocomposites depend on the organomodifier content: increased organomodifier content leads to a more pronounced catalytic effect and more intensive char formation [29]. Figure 2.5 shows the effect of surface modification on the HRR behavior of PP. Incorporating organomodified montmorillonite (OMMT) decreased the PHRR the most owing to the nanodispersed clay and the catalytic properties of the organomodifier.

The second most important factor in improving nanocomposite fire retardancy is clay loading. Unlike CNT loading, increasing clay loading improves nanocomposite fire retardancy, and there is no optimal clay loading in the range <15 wt% [33, 34]. It is difficult to form a crack-free clay-network layer. Therefore, the main flame-retardancy mechanism is through the formation of a barrier against the heat source instead of gases. Photos of residues obtained from degraded PS/OMMT samples containing various OMMT contents are shown in Fig. 2.7. The residues from the degraded PS/OMMT samples containing 6- and 15-wt% OMMT show cracks. Thicker floccules can be obtained by adding more clay. The formation of thick floccules can significantly decrease HRR. Clay-based nanocomposite flame retardancies could be further improved if polymer-clay nanocomposites could be tuned to form more stable crack-free networks during burning.

The effect of nanomorphology on flame retardancy has previously been discussed in the literature [32, 43, 44]. Most researchers have concluded that polymer/clay nanocomposites should at least exhibit PHRR reduction if nanomorphology is achieved through exfoliation and intercalation. The difference in nanomorphologies does not significantly affect polymer/clay nanocomposite flame retardancy. Nanocomposites can be obtained by organomodifying clays, and is easily achieved through melt-compounding. However, organomodified clay surfaces degrade at high temperatures, rendering organomodification problematic in melt-compounding and decreasing nanocomposite flame retardancy [37].

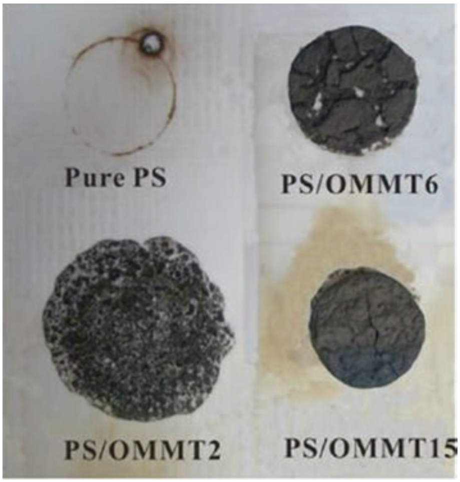


Fig. 2.7 Digital *photos* showing the residue morphology of different PS/OMMT composites after degraded at 400 ºC for 3 h (reprinted from [33])

2.3 Polymer Nanocomposites Combined with Conventional Fire Retardants

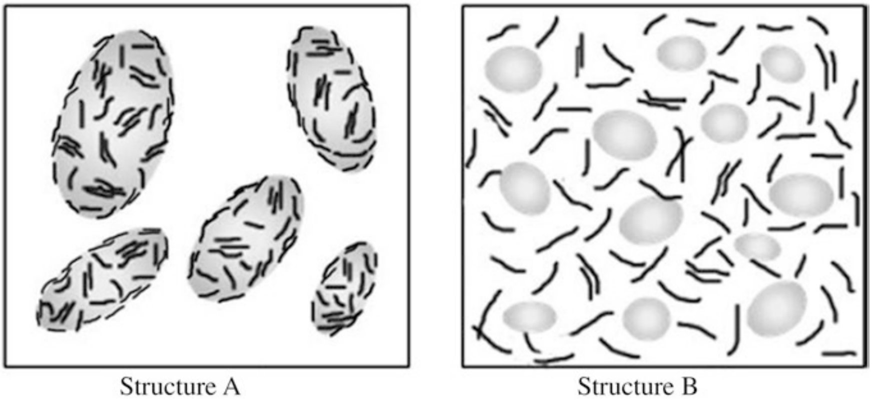
Although the HRRs polymer-nanocomposite-only fire retardants are greatly reduced, the total amount of heat released remains unchanged so that the nanocomposites burn slowly once they ignite but do not self-extinguish. This is why nanocomposites themselves have not been used as commercial products, which must pass strict regulatory tests. It is expected that combining polymer nanocomposites with conventional fire retardants can fully exploit the fire-retardancy mechanism of nanofillers; i.e., the slow burning and the mechanical reinforcement of char layers. In fact, the material produced by combining the EVA nanocomposite with conventional aluminum hydroxide is used as a cable cover. Adding only 5 wt% organoclay can reduce the amount of aluminum hydroxide used (20 wt%) without deteriorating flame retardancy. In addition, it can improve the mechanical properties of the cable because less aluminum hydroxide is used and owing to the reinforcement of the clay. This ternary system was developed to reduce the amount of halogenated flame retardant used and to develop halogen-free fire retardants.

There are uncountable combinations of fire retardants. Some combinations synergistically improve fire retardancy but others antagonistically affect it. There is a vast amount of research available on the synergistic effects of combining nanofillers and conventional fire retardants on fire retardancy, so knowing the results and the fire-retardancy mechanisms will be useful for developing better fire retardants. Combining halogenated additives with antimony oxide (Sb_2O_3) positively affects fire retardancy. The Sb_2O_3 reacts with the hydracids generated by the halogenated additives to form antimony oxyhalides, which are much heavier than the native hydracids, thus prolonging their residence time in the flame. From this example, we can infer that clay might enhance the halogenated-additive effect because the clay can act as a barrier, delaying the burning and prolonging the residence time of hydracids. Combining polymer-clay nanocomposites with melamine cyanurate showed the antagonistic effect [45–47]. The melamine cyanurate improves LOI and UL classification by facilitating the polymer to drip away from the fire source. However, adding nanoclay increases the polymer melt viscosity; hence, the polymer in this polymer nanocomposite system will not drip away from the fire source, and this ternary system cannot pass the UL94 regulatory tests. Many previously reported combinations are discussed in the following sections.

2.3.1 Nanocomposites Combined with Halogenated Flame Retardants

Most research has been conducted on nonhalogenated flame retardants because halogenated ones have been proscribed. However, the latter are being reevaluated owing to their recyclability and highly effective flame retardancies. The European Union RoHS directive prohibited the use of PPB and PBDE. Decabromodiphenyl ethane (DB) was developed in the 1990s. The DB molecule does not contain any ether bonds and will not generate polybrominated dibenzofurans (PBDBFs) or polybrominated dibenzo-*p*-dioxin (PBDD). Further, DB is recyclable and is therefore widely used as a halogenated flame retardant.

Nanofiller distribution is the key point to obtaining synergistic effects between the nanofiller and a conventional flame retardant. Figure 2.8 shows filler distributions typical for ternary materials. The nanofiller will be incorporated into the fire retardant (structure A) if the nanofiller is more compatible with the fire retardant than with the matrix; that is, if the nanofiller shows better wettability with the fire retardant than with the matrix. The nanofiller will be dispersed into the matrix instead of the fire retardant (structure B), on the other hand, if the nanofiller shows


Structure A

Structure B

Fig. 2.8 Schemes for the two different model structures: *structure A* (nonofiller is incorporated to fire retardant) and *structure B* (nanofiller is dispersed in a matrix) (reprinted from [48]) better wettability with the matrix than with the fire retardant. For instance, the clay does not catalytically affect the matrix in structure A, and the thick, uniform char layer (which is the main fire-retardancy mechanism for clay) cannot form because the clay is poorly distributed. Therefore, structure B is preferable to structure A for enhancing ternary-composite flame retardancy. Chen et al. investigated the relation between organoclay distribution and flame retardant PP flammability for the material system consisting of PP, brominated epoxy resin/antimony oxide (BER-AO) and OMMT [48]. OMMT was incorporated into BER in the absence of polypropylene-graft-maleic anhydride (PP-g-MAH), which can increase PP polarity and aid OMMT dispersion. Adding PP-g-MAH can change the structure from A to B. Adding OMMT to the PP/BER/AO/OMMT system (structure A) worsened its flammability, and the system failed the UL-94 tests. In contrast, the PP/PP-g-MAH/BER/AO/OMMT system (structure B) showed V-0 classification. Adding OMMT significantly reduces the PHRR and THR of structure B, indicating a synergistic effect between the clay and the halogenated flame retardants. Clay distribution must be carefully considered when designing effective ternary composites.

Zanetti et al. also showed that combining nanoclay and a halogenated flame retardant produced a positive effect [49]. Adding 22 wt% DB and 6 wt% AO decreased the average HRR from 279 to 245 kWm^{-2}. They presumed that faster combustion is presumably responsible for the inability to observe synergy in the polymer, thus nullifying the retarding effects of both HBr generated by DB and the radical inhibitor $SbBr_3$ generated by DB-AO. Adding OMMT to PP/DB-OA systems, on the other hand, decreased the average HRR to 107 kWm^{-2} because of the slow burning effect achieved by adding clay. The free-radical reactions that propagate the flame were thus slow enough to enable the DB-generated HBr to slow the combustion. PP [50], PMMA [51], PS [52, 53], and PA6 [47] all showed the same synergistic effect. The clay-produced char layer can not only act as a barrier against heat and mass transport but also reinforce the halogenated-flame-retardant effect. This synergistic mechanism is not specific to these polymers; thus, it opens the possibility of formulating self-extinguishing materials from large classes of polymer nanocomposites and halogenated flame retardants [51].

Wilkie et al. combined CNTs with clay to develop a synergistic material for the PS/BER/AO system [52]. The BER and multiwalled nanotubes (MWNTs) showed better synergy than the BER and clay for improving the flame retardancy of the system possibly because the CNT-produced surface layer was compacter and denser than the clay-produced char layer. Nanofillers and halogenated fire retardants show synergistic effects as long as the surface-barrier layer is formed, and the synergistic effects depend on the nanofiller-produced-surface quality; i.e., compactness and absence of cracks.

2.3.2 Nanocomposites Combined with Phosphorus and Intumescents

Phosphorus-based fire retardants act in the gaseous and condensed phases, and their main fire-retardancy mechanism is through the formation of a char layer, which acts as

Table 2.1 Cone calorimetric results for PP and its composites. *Source* Reference [54]

Formulation of PP and its composites	t_{ign} (S)	t_{PHRR} (S)	PHRR ($\mathrm{kWm^{-2}}$)	THR ($\mathrm{MJm^{-2}}$)
PP(100)	37 ± 4	189 ± 12	363 ± 17	56 ± 2
PP(67)/PP-*g*-MAH(5)/IFR(28)	33 ± 3	435 ± 20	62 ± 5	24 ± 1
PP(67)/PP-*g*-MAH(5)/IFR(25.5)/ CNT(2.5)	33 ± 3	189 ± 15	145 ± 8	54 ± 1
PP(67)/PP-*g*-MAH(5)/IFR25.5)/ OMMT(2.5)	31 ± 2	360 ± 18	45 ± 5	18 ± 3
PP(67)/PP-*g*-MAH(5)/IFR(25.5)/ LDH(2.5)	30 ± 2	300 ± 15	64 ± 6	20 ± 3
PP(67)/PP-*g*-MAH(5)/IFR(25.5)/ POSS(2.5)	32 ± 2	375 ± 16	55 ± 5	16 ± 2

a barrier. Phosphorus-based fire retardants often contain intumescent flame retardants to improve the insulator properties of the former; hence, we categorize phosphorus and intumescents together. Phosphorus-based fire retardants and nanofillers both act as barriers during combustion; therefore, adding nanofillers to composites containing phosphorus-based fire retardants will either reinforce or deteriorate the barrier effect.

Du et al. investigated ternary systems composed of PP, intumescent flame retardant (IFR), and various nanofillers such as CNT, OMMT, layered double hydroxide (LDH), and polyhedral oligomeric silsesquioxane (POSS) [54]. They melt-blended ternary composites and showed that all the nanofillers except LDH had dispersed well throughout the matrix, not throughout the IFR. The LDH-containing composites showed intercalated and even some larger agglomerated LHD tactoids in the majority of the LDH. Their cone calorimetry results are listed in Table 2.1. Adding nanofillers to the PP/IFR composite did not vary the ignition temperature, whereas it either improved or deteriorated the PHRR and THR in cone calorimetry tests. Adding CNTs to the PP/IFR systems produced antagonistic effects; that is, adding CNTs to polymer/IFR systems increases the PHRR, indicating accelerated burning [54–56]. Istiman et al. also found that the PMMA/organophosphorus/CNT system showed the same phenomena; i.e., antagonistic effects [56]. The residue observed after the cone calorimetry test showed that adding CNTs to the PP/IFR system had generated cracks on the residue surface and that the CNTs had also inhibited intumescence. The intumescence had disrupted the formation of a uniform CNT network on the surface, while the CNTs had inhibited IFR swelling; hence, combining the CNTs with the IFR showed antagonistic effects. OMMT showed the best synergistic effect in reducing the PHRR. Substituting 2.5 % IFR for the OMMT decreased both the PHRR and the THR. Adding the OMMT reinforced the char layer, which generated the synergistic effect. Ma et al. explained that the intumescent-generated phosphoric acid had probably reacted with montmorillonite to form silicoaluminophosphate (SAPO) [57]. In addition, organomodifier decomposition produces strongly acidic catalytic sites, which may further promote oxidative dehydrogenation crosslinking charring. These phenomena enhance the efficiency of the char layer protecting against heat transfer and mass (i.e., oxygen and decomposed gas) transport.

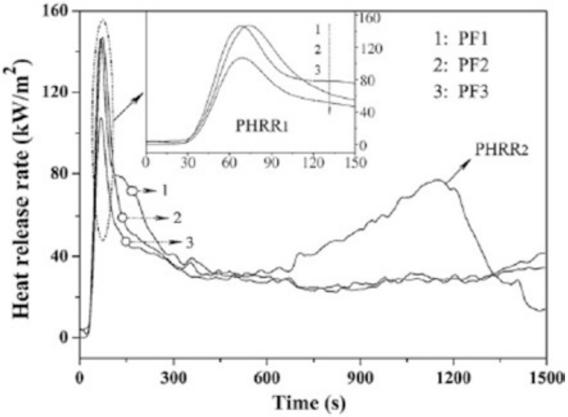


Fig. 2.9 HRR curves of PP/IFR(nitrogen-phosphorus)(PF1), and PP/IFR/OMMT(PF2, PF3). The OMMT content of PF2 and PF3 are 1.8 and 2.6 wt%, respectively (reprinted from [58])

The phosphorus and clay showed synergistic effects in improving fire retardancies of ABS [57], PP [58, 59], PE [60], and PA6 [61]. Ma et al. investigated the fire retardancy of the ABS/poly (4,4-diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate) (PDSPB)/OMMT ternary system [57]. Adding 30 wt% PDSPB reduced the PHRR from 930 to 388 kW/m^2 during the cone calorimetry test. Interestingly, adding 18 wt% PDSPB and 2 wt% OMMT further reduced the PHRR to ~370 kW/m^2, indicating that using only 2 wt% OMMT can save the use of >10 wt% PDSPB. The mechanical properties should be improved by adding clay because it can reduce the amount of IFR used and because IFR deteriorates the mechanical properties of the materials. Du et al. examined the fire retardancy of the PP/IFR/organobentonite composite [58]. Adding 28 wt% IFR enabled the composite to achieve V-0 classification during the UL-94 test and increased the composite LOI from 18.4 to 30.7 %. Adding 2.6 wt% organobentonite increased the ternary-composite LOI to 32.8 %. Figure 2.9 shows the HRR curves for the PP/IFR and ternary composites. The HRR for the PP/IFR (PF1) shows two peaks at 33 and ~1,200 s. The intensity of the first peak attributable to HRR can be reduced by adding IFR, which forms the surface char layer. Fine cracks are gradually produced on the char layer, collapsing the char structure while the material absorbs heat. The HRR shows the second peak when the surface char layer collapses. The HRR for the PP/IFR/organobentonite system did not show the secondary peak, which is undesirable for fire retardants. The clay improves the mechanical strength of the char layer and suppresses its collapse during combustion. Huang et al. also demonstrated the synergistic effects for the PE/diphenylmethanamine spirocyclic pentaerythritol bisphosphonate (PSPD)/OMMT system [60]. The PE/PSPD(15)/OMMT(5) reduced the PHRR by ~51 % more than pure PE did, although the PHRR of the PE/PSPD(20) was reduced by only 26.8 %. Again, adding clay contributed to the formation of the high-strength char layer, reducing the intensity of the first peak attributable to the PHRR and suppressing secondary combustion.

The IFR and clay do not always show synergistic effects, and some of minor fire retardant effects were observed for PS [62], PP [63], and PMMA [56]. Chen et al. investigated the flame retardancies of PS/PDSPB/OMMT composites. Incorporating 20 wt% PDSPB into the PS reduced the PHRR from 739 to 502 kW/m^2. However, adding 4 wt% OMMT to the PS/PDSPB(20) increased the PHRR to 527 kW/m^2. The OMMT had been incorporated into and restricted in the PDSPB phase (Fig. 2.8, structure A); thus, the uniform char layer could not be obtained, and the clay and IFR did not show any synergistic effects. Szustakiewicz et al. found that the PP/APP/OMMT system did not show any synergistic effects [63] and concluded that incorporating OMMT had worsened the PP flame retardancy when intercalated or exfoliated nanomorphology was not obtained. Istiman et al. added CNTs or OMMT to try to improve the flame retardancy of the PMMA/organophosphorus (OP) system [56]. Incorporating CNTs into the PMMA/OP system deteriorated its flame retardancy through adverse effects, and incorporating OMMT into it only slightly reduced the PHRR from 63 to 66 %. The clay interacted with the PMMA less than with the other polymers; thus, the compact char layer could not form in the PMMA/OP/OMMT system. An alternative approach is thus required in order to improve PMMA flame retardancy.

Polymer/IFR/clay ternary composites show excellent fire retardancy as long as nanomorphology is formed and the clay is well distributed throughout the polymer matrix. Optimizing the clay content improves the flame retardancy of this system. Wilkie et al. surveyed thirty kinds of phosphorous that could be used to improve the fire retardancy of this system and investigated which clay and phosphorus combinations showed the best synergistic effects during the screening test [64]. Table 2.2 shows part of their results. Adding 30 wt% phosphorus fire retardant clearly reduced the PHRR by 64 % for resorcinoldiphosphate (RDP) and 38 % for trixylyphosphate (TXP). Incorporating clay further decreased the PHRR, and the optimal clay load was 5 wt% for both systems. Using the 5 wt% clay load decreased the PHRR by 92 %, which was the best PHRR reduction. Hu et al. also determined the optimal clay loads to enhance the synergistic effects between clay and various IFRs including APP and pentaerythritol (PER) [65]. The synergistic

Table 2.2 Optimal clay content for PS/resorcinoldiphosphate (RDP) and PS/trixylyphosphate (TXP). *Source* Reference [58]

Sample	t_{ign} (S)	PHRR kW/m^2 (% redution)	Total heat released (MJ/m^2)
PS	62	1419	109.7
PS/RDP 30 %	77	499 (64)	41
PS/RDP 30 %/clay 3 %	75	358 (74)	42.3
PS/RDP 30 %/clay 5 %	55	110 (92)	43.1
PS/RDP 30 %/clay 10 %	63	307 (78)	44.7
PS/TXP 30 %	57	864 (38)	53.9
PS/RDP 30 %/clay 5 %	38	313 (78)	45.5
PS/RDP 30 %/clay 10 %	59	372 (73)	49.4

effect is related to the ratio of MMT to IFR. The negative effect of adding clay is that the NH_3 is prevented from swelling the char, which is similar to the negative effect of adding the CNTs. The negative effect may outweigh the positive one (i.e., producing the char layer and reinforcing it through crosslinking) when the amount of clay added exceeds a specific value.

Other additives can be combined with polymer nanocomposites to enhance the synergistic effects in order to improve the flame retardancies of polymer/phosphate systems. Cinausero et al. improved the fire retardancy of the PMMA/APP system by adding oxide nanoparticles [66]. Alumina and silica particles, whose average diameter was 12 nm, were added to the PMMA/APP. As-prepared hydrophilic metal oxide particles were used, and some of them were surface-treated to make them hydrophobic and thus more compatible with the polymer, improving the metal-oxide dispersion throughout the polymer and the molten-metal-oxide migration. The cone calorimetry results are shown in Fig. 2.10. Alu-C8 in Fig. 2.10 indicates the surface-modified alumina particles, and Sil indicates the untreated silicate ones. Although it is difficult to improve PMMA flame retardancy, combining metal oxide with APP showed the synergistic effect, and the PHRR was reduced by more than 50 %, as shown in Fig. 2.10. The surface-treated hydrophobic silica nanoparticles showed the best flame retardancies. The PMMA/AP/Sil-C8 system had developed a smooth, crack-free residual char layer, while the other system had developed a residual char layer showing numerous cracks, meaning that adding Sil-C8 can form a compact char layer, which can improve the barrier properties. These results showed that the silica and APP had strongly interacted. Cinausero et al. mainly ascribed the flame retardancy to the

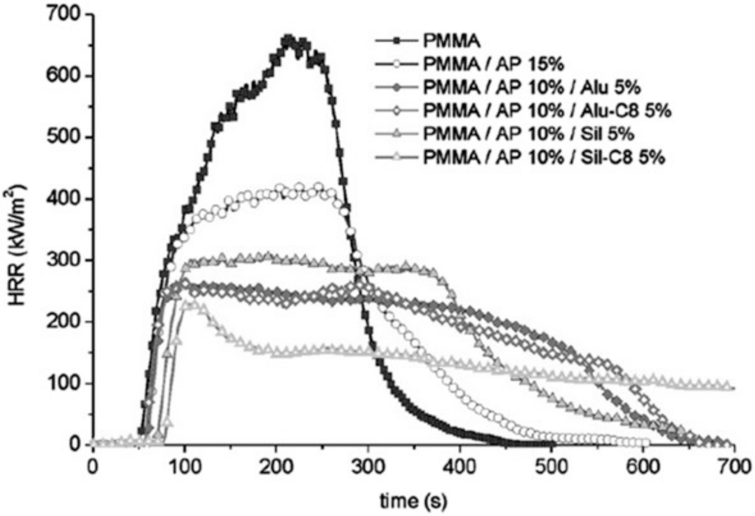


Fig. 2.10 Effect of oxide nanoparticles on fire properties of PMMA/APP composites (reprinted from [66])

crystalline silicon metaphosphate (SiP_2O_7) phase, which contributed to charring and promoted the formation of an efficient barrier. This method (i.e., combining APP with silica) can work efficiently for polymers such as PS. Their results indicate that the interaction between conventional fire retardants and other additives is important in improving fire retardancy.

Combining IFR with metal oxides such as antimony oxide (Sb_2O_3) shows synergistic effects in improving fire retardancy. For instance, adding 2 wt% Sb_2O_3 increased the LOI of the PP/IFR system from 27.8 to 36.6 % [67]. Li et al. presumed that this was because Sb_2O_3 could react with APP to form the stably crosslinked charred layers, which forms a barrier against heat transport and oxygen diffusion. Wu et al. examined nine metal oxides for their potential synergistic effects for improving the flame retardancy of the PP/IFR system [68] and found that the PP/IFR combined with Ni_2O_3 showed the best performance in their experiments.

2.3.3 Nanocomposites Combined with Metal Hydroxides

Metal hydroxides are widely used in fire retardants because they are safe and inexpensive and because they reduce the amount of smoke produced in fires. However, high loads (>60 wt%) are mandatory to satisfy the V-0 classification, which is required for most fire retardants, and such high loads degrade mechanical properties, resulting in inflexible materials. The main purpose of combining nanofillers with metal hydroxides is to reduce the metal-hydroxide load without deteriorating flame retardancy. Clays and metal hydroxides are often combined to produce the EVA matrix, which is used for cable outer sheaths [69–72]. Unlike the polymer/phosphorus/nanofiller system, which shows an antagonistic effect, the polymer/metal hydroxide/nanofiller system has not shown an antagonistic effect to date. The nanofiller is not incorporated into the metal hydroxide as a matter of course; it is well dispersed throughout the polymer matrix.

Beyer investigated the fire retardancy of EVA/alumina trihydrate (ATH) combined with either nanoclay or CNTs [69]. The cable outer sheath is often composed of 35 wt% EVA and 65 wt% ATH. The fire-retardant composite showed a PHRR of ~200 kW/m^2 during cone calorimetry at 50 kW/m^2 heat flux. Replacing 5 wt% of the ATH with nanoclay reduced the PHRR to 100 kW/m^2. The rigid char layer that had formed for the EVA/ATH nanocomposites showed fewer cracks than that which had formed for the EVA/ATH compound, and it contributed the reduction in the PHRR during cone calorimetry. Beyer showed that ~78 wt% ATH was required for the EVA(35)/ATH/(60)/nanoclay(5) nanocomposite to achieve the same flame retardancy (*i.e.*, PHRR: 100 kW/m^2). Furthermore, the ATH content could be decreased from 65 to 45 wt% by adding only 5 wt% OMMT in order to maintain a sufficient peak heat release (200 kW/m^2). This wide range of PHRR reduction can contribute to improving material processability and mechanical properties.

Table 2.3 Optimal loading level for EVA/metal hydroxide/OMMT ternary composites. *Source* Reference [70]

Sample	LOI (%)	UL-94
EVA	19.5	–
EVA/MH(50)	27.5	V-0
EVA/MH(49)/Nanoclay(1)	33.5	V-0
EVA/MH(48)/Nanoclay(2)	34.5	V-0
EVA/MH(46)/Nanoclay(4)	31.0	V-0
EVA/MH(44)/Nanoclay(6)	30.5	V-0
EVA/ATH(50)	25.5	–
EVA/ATH(49)/Nanoclay(1)	27.0	V-0
EVA/ATH(48)/Nanoclay(2)	28.0	V-0
EVA/ATH(46)/Nanoclay(4)	26.0	–
EVA/ATH(44)/Nanoclay(6)	25.5	–

Yen et al. discussed the optimal loads for the EVA/ATH/clay and EVA/magnesium hydride (MH)/OMMT systems, as shown in Table 2.3 [60]. They used 50 wt% total filler content and replaced part of the ATH or MH with a small amount of OMMT. Replacing the metal hydroxide with OMMT increased the LOIs of both material systems; however, the LOIs stopped increasing when 2 wt% of the metal hydroxide had been replaced with OMMT because less metal hydroxide remained in the systems. Yen et al. suggested that adding OMMT reinforced the surface char layer acting as the insulation and that the formed layer had responded to the synergistic effect of flame retardancy and had suppressed the smoke from the EVA blends. Ye et al. showed that the CNT-based nanocomposite was synergistic [73]. Substituting 2 wt% MWNTs with metal hydroxide (MH) increased the EVA(50)/MH(50) LOI from 34 to 39 %. Replacing 2 wt% MWNTs with MH optimized the fire retardancy, and further replacing MWNTs decreased the LOI.

Hong et al. [74] developed fire-retardant PP-based composites to replace polyvinyl chloride (PVC), which is a cable insulator that shows excellent fire retardancy but poses health and environmental problems. Adding mineral filler to PP drastically decreases material elongation. They blended PP/poly(ethylene-co-propylene) (EPR) with mineral fillers and OMMT to retain high material elongation. The PP(36)/MDH(60)/OMMT(4) composite showed 210 % elongation at break and 27 % of the LOI. Knog et al. investigated the effects of structural iron on the fire retardancy of the PP/ATH/OMMT ternary system, as shown in Table 2.4 [75]. The iron strengthened the synergistic effect between the clay and the ATH and trapped some of the free radicals, which enhanced the thermal stability of the system and the char ratio [37, 75].

PE and high-impact polystyrene (HIP) combined with metal hydroxides and OMMT have also shown synergistic effects [76, 77]. Combining PE with 2.5 wt% inorganic clay and 20 wt% ATH reduced the PHRR 73 % more than using only pure resin [76]. This PHRR reduction is comparable to that obtained by combining PE with only 40 wt% ATH. Istman et al. solution- and melt-mixed HIP/ATH/nanoclay composites and discussed the relations between nanofiller

Table 2.4 Effect of structural iron on flammability of PP/ATH/OMMT composites. *Source* Reference [75]

Code	PP (wt%)	ATH (wt%)	Fe-OMT (wt%)	Na-OMT (wt%)	LOI	UL-94
PP0	100				17	Buringing, drip
PP1		50			23	Buringing, drip
PP2		48	2		25	V2
PP3		45	5		27	V1
PP4		43	7		29.5	V0
PP5		48		2	23	Buringing, drip
PP6		45		5	23.5	Buringing, drip
PP7		43		7	24	Buringing, drip

flame retardancies and dispersions [77]. Solution-mixing produced the nanocomposite. Melt-mixing, on the other hand, produced the microcomposite. The nanocomposite PHRR decreased twice as much as the microcomposite one during cone calorimetry. In addition, the nanocomposite mechanical properties were superior to the microcomposite ones. Incorporating 3 wt% well-dispersed nanoclay showed a similar effect on decreasing the PHRR as adding 15 wt% ATH. The LOI of the solution-mixed HIP(62)/ATH(35)/clay(3) was 22 %, indicating that more ATH was required in order to achieve V-0 classification during the UL test.

2.3.4 Other Combinations

The previous sections mainly describe combining CNT- and clay-based nanofillers with conventional fire retardants. However, many other combinations can effectively improve polymer flame retardancy. Goodariz et al. recently reported that calcium carbonate ($CaCO_3$) nanoparticles could improve both thermal and thermo-oxidative stability [78]. Table 2.5 shows the mechanical properties and fire retardancy of the composite prepared with DB, clay, and $CaCO_3$. Goodariz et al. used

Table 2.5 Remarkable improvement for fire properties by incorporating $CaCO_3$ nanoparticle. *Source* Reference [78]

Sample	LOI (%)	UL-94	PHRR reduction (%)	Young modulus (MPa)	Tensile strength (MPa)
PP	17.4	Buring	–	1,960	40
PP(85)/DB(11.25)/AO(3.75)	24.3	V-2	53	1,887	28.81
PP(95)OMMT(5)	22.7	Buring	36	3,652	43
PP(95)/$CaCO_3$(5)	23.6	V-0	59	3,721	46.32
PP(95)/OMMT(5)/$CaCO_3$(5)	29.2	V-0	76	4,365	55.21

~50 nm-diameter $CaCO_3$ nanoparticles and used a titanate coupling agent to modify the nanoparticle surfaces. Surprisingly, incorporating 5 wt% $CaCO_3$ into the nanoparticles produced self-extinguishing PP, although the $CaCO_3$ fire-retardancy mechanism is unclear. The $CaCO_3$ in PP could retard polymer oxidation [79], which might contribute to PP fire retardancy. The fire retardancy of PP combined with 5 wt% $CaCO_3$ was comparable with those of PP combined with DB and AO, and the mechanical properties of the PP/$CaCO_3$ composites were superior to those of the PP/DB/AO composites. Simultaneously incorporating $CaCO_3$ and OMMT into PP produces a synergistic effect that improves both the PP fire retardancy and mechanical properties.

Incorporating a combination of nanofillers into polymers reportedly improves polymer fire retardancy [69, 80–82]. Ma et al. incorporated clay and MWNTs into ABS resin and reduced the flammability of the nanocomposites more than incorporating either the clay or the MWNTs did. The EVA/clay/MWNT and PP/clay/MWNT ternary composites showed the same phenomenon [82]. Further, the MWNTs were linked between clays, indicating that the clay and MWNTs had strongly interacted, enabling the formation of a crack-free compact char layer. They used a one-to-one ratio of clay and MWNTs. The optimal ratio of MWNTs to clay for improving flame retardancy does exist, and further research must be conducted to determine the exact ratio.

2.4 Fire-Protective Coatings

Modifying material surfaces is an effective method of strengthening barriers against gas and heat transfer inside materials; hence, surface-modified materials are also fire retardants. Applying a flame-retardant coating is one of the most effective and economical methods of protecting substrates from fire damage. Polymer bubbling causes the nanofillers inside materials to migrate to the surface, where they then act as a barrier against heat and mass transport and can reduce the heat intensity during combustion. It is expected that nanofiller-based coatings more efficiently reduce material flammability than materials containing nanofillers.

Flame-retardant coatings are classified as intumescent and nonintumescent systems. Intumescent coatings are usually applied to wood and steel in order to protect the substrates from the fire. Intumescent coatings generate char and swell during combustion. The swelled char layer acts as a heat-insulation material, which can protect the substrate from the fire. There are numerous nonintumescent coatings such as halogen-based, phosphorus-based, and inorganic-additive-incorporated systems. Nonintumescent systems are significantly less efficient than the intumescent flame-retardant (IFR) coating in reducing polymer flammability. There are already comprehensive reviews on intumescent [83] and nonintumescent [84] systems, so we will briefly introduce the IFR coating and mainly highlight the nanotechnology used to produce it.

2.4.1 Intumescent Coating

Epoxy, acrylic, PVA, urethane, or silicon polymers are used as IFR binders. Some of fillers such as TiO_2 are added to increase the fire-retardant efficiency. The IFR coating is sprayed, dipped, or brushed onto the substrate to form a layer ranging from a few tens to hundreds of microns thick. The IFR coating improves the bulk-material flame retardancy without changing the mechanical properties and is aesthetically attractive. However, it is not reliable long term because the coating poorly adheres to the substrate surface, leading to delamination, which deteriorates or defeats the effectiveness of the IFR. In addition, the IFR absorbs water and ultraviolet (UV)-filtered light, further deteriorating it [85]. Therefore, an additional surface coating is required in some cases.

Many methods of coating including UV-curing, physical and chemical vapor deposition, and layer-by-layer (LBL) assembly have previously been developed. UV-curing is an attractive method because it consumes small amounts of energy and because the coatings are rapidly cured (in a few seconds). However, it is difficult to use this method in order to coat complex-shaped samples because some or part of the samples might not be exposed to UV light. Chemical vapor deposition has been used to improve the flame retardancy of textile materials and electrical devices [86].

Although LBL is a highly tailorable method of coating, it is time consuming because the substrate must be repeatedly dipped and washed until the desired number of bilayers has been deposited onto it. Therefore, this method is only used for lab-scale modeling and cannot be practically applied to large-scale production. Dipping and spraying are the simplest, most inexpensive methods; hence, they are preferable for practical large-scale production.

Bourbigot et al. and Wang et al. have dipped or sprayed substrates to develop an effective method of IFR coating [85, 87–99]. Bourbigot et al. investigated the fire retardancies of PP and PC substrates coated with either PVA-based IFR containing APP, pentaerythritol (PER), and melamine or an acrylic-resin-based formulation containing PER, silica, and phosphoric acid. Both coatings enable PP and PC to achieve V-0 classification during UL-94 tests [87]. Figure 2.11 shows the IFR-coated-PP residue after the cone calorimetry test. The varnish coating had expanded more than the PVA one, so the varnish coating is more fire-retardant efficient than the PVA one. The 200-μm-thick PP-coating PHRR was reduced to 143 and 4 kW/m^2 for the PVA

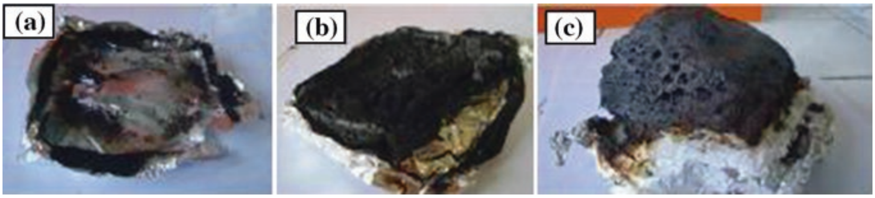


Fig. 2.11 Pictures of residues of PP (**a**), PP coated (**b**), PP varnish (**c**) (reprinted from [87])

and varnish coatings, respectively. The varnish coating can swell enough to act as an insulating barrier, completely protecting the polymer from the fire source. The 1.6-mm-thick PP and PC samples had to be coated with 158- and 42-μm-thick layers of varnish, respectively, to achieve the V-0 rating [85]. The coating worked better on the PC substrate because the PC had produced char during combustion and had interacted with the coating. The PP, on the other hand, had melted and vigorously burned without forming char. The varnished PP and PC fire retardancies slightly decreased when the varnished substrates were exposed to UV-filtered light. Bourbigot et al. attributed the decreased fire retardancies to decreased varnish adhesion rather than to chemical modification of the varnish through FTIR and TGA analyses.

2.4.2 Nanocoating

Solution casting, which is a method of producing nanocomposites with high filler contents, has recently been developed. For instance, solution-casting can be used to produce 100 % clay paper. Paper produced from CNTs is called “CNT buckypaper.” Such high-nanofiller-loaded materials may be applied as coatings reduce substrate flammability. Solution-cast nanocomposites are different from bulk ones because the fillers do not migrate within the composites and because strong nanofiller networks can always be formed in nanocoatings. Preparing nanodispersed slurry is the most important step in nanocoating because nanocoating highly depends on slurry dispersion. The nanocoating can then be dipped, sprayed, or deposited layer by layer onto the substrate. Solution-casting or vacuum filtration can then be used to fabricate the nanofiller barrier film.

Platelet materials such as clay or graphene are preferable for improving gas barrier properties because they force permeating molecules to travel extended paths referred to as “tortuous pathways.” The gas permeability of the thin coating layer composed of aligned platelets is some orders of magnitude lower than that of the virgin material, depending on the aspect ratio and filler content [90]. In fact, numerous researchers have used clay [90–96] and graphene [8, 97] to produce nanodispersed films showing extraordinary mechanical and gas-barrier properties. Two important fire-retardancy mechanisms involve reducing fuel-gas diffusion to the fire source and reducing oxygen diffusion inside materials. Therefore, multifunctional nanocoatings are expected to contribute flame retardancy.

The method of producing clay and polymer building blocks is depicted in Fig. 2.12. Unmodified clay is naturally hydrophilic, so a homogenizer or an ultrasonicator can be used to easily disperse it in water or aqueous solutions. Dispersed clay particles then absorb polymer onto their surface when nanodispersed slurry is poured into an aqueous solution containing a water-soluble polymer such as PVA. Polymer absorption can stabilize the clay dispersion because each polymer-coated clay particle shows steric repulsion. The polymer-coated-clay solution is then available for making paper, painting, spraying, and doctor-blading. Walther et al. produced nacre-inspired biomimetic clay films as hard segments and either PVA or chitosan as block binders [93, 94]. The biomimetic film fabricated with MMT and

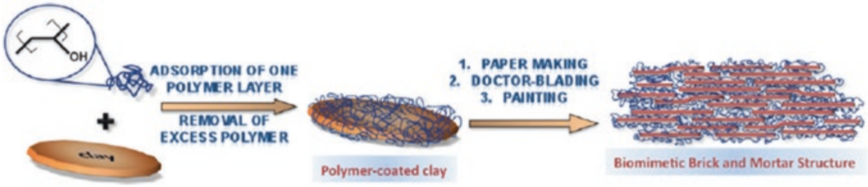


Fig. 2.12 Strategy toward the preparation of biomimetic self-assembled brick and mortar structures based on common, scalable, and simple processing method (reprinted from [93])

chitosan showed not only high mechanical stiffness (25 GPa) and tensile strength (320 MPa) but also shape-persistent fire-blocking. The film containing 40 wt% clay hardly burned while exposed to a gas-torch flame and instantly self-extinguished.

Nanocoatings have recently been used to try to reduce polymer flammability. Laauchi et al. used LBL deposition to form a nanodispersed layer composed of clay and polyallylamine hydrochloride (PAH) in order to improve substrate flame resistance [98, 99]. The thickness of the $(\text{PAH-MMT})_n$ coating increased with the number of bilayers deposited, and reached 5 μm after 20 bilayers had been deposited. The subscript n means the number of LBL-deposited bilayers. Figure 2.13 shows HRR curves for uncoated and coated PA-6 during a cone calorimetry test. Although the PA-6-$(\text{PAH-MMT})_5$ and PA-6-$(\text{PAH-MMT})_{10}$ HRRs are higher than the uncoated PA-6 one, indicating that the former two combust faster than the latter, the PA-6-$(\text{PAH-MMT})_{20}$ HRR is much lower than the uncoated PA-6 one. The PHRR was reduced by 62 % when only a 5-μm-thick nanolayer was coated onto the PA-6. A >100-μm-thick IFR coating must be coated onto the PP to reduce the PP PHRR to the same level. The nanocoated polymer obviously exhibited highly efficient flame retardancy. Although the fire-retardancy mechanisms for the nanocoating and IFR coating are completely different, both act at the condensed phase, reducing the HRR without changing the THR. IFR swells during combustion and acts as insulation, reducing the amount of heat transported into the substrate. The nanocoating, on the other hand, does not swell like IFR. Therefore, the main nanocoating fire-retardancy mechanism reduces the amounts of fuel gas and oxygen transported to the fire and into the material, respectively. The clay-platelet shape reduces the gas and oxygen diffusion rates by several orders of magnitude owing to the tortuous effect. The nanocomposite layer cannot retard the fire if it fractures during combustion, as in the case of PA-6-$(\text{PAH-MMT})_5$ and PA-6-$(\text{PAH-MMT})_{10}$ (Fig. 2.13). In fact, Laauchi et al. showed that the char layer cracked after the test for PA-6-$(\text{PAH-MMT})_{10}$, and they concluded that the most important factor for producing flame retardant nanocoating is to a form uniform nanodispersed layer that does not fail during combustion. Choosing the proper clay and polymer clay binder and producing a sufficiently thick coating are all important factors in obtaining high-strength char during combustion.

Laufer et al. used LBL deposition to develop a completely green coating composed of clay and chitosan [100]. They applied the coating to a polylactic acid film and polyurethane (PU) foam to improve the oxygen barrier and fire retardancy. Notably, a <100-nm-thick clay-chitosan nanocoating reduced the oxygen

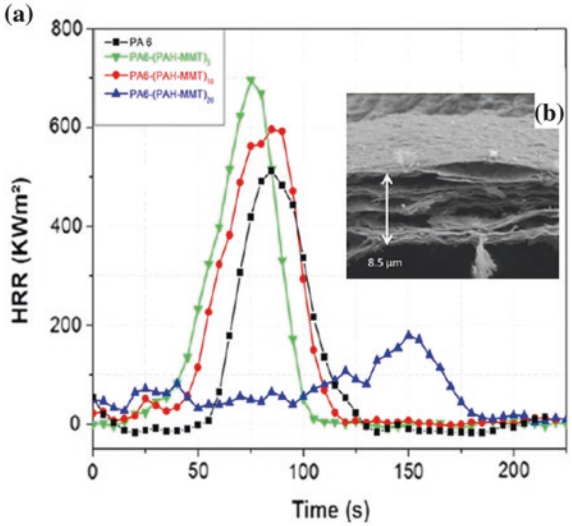


Fig. 2.13 Heat release rate curves as a function of time for coated and uncoated PA6 samples (**a**), cross-section image of 20 BL film residue after burn testing (reprinted from [99]) (**b**)

permeability of a 0.5-mm-thick PLA film by four orders of magnitude. In addition, the 30-nm-thick green nanocoating reduced the PHRR by 52 % and eliminated the secondary peak in the HRR curve. They demonstrated that environmentally benign nanocoatings can prove beneficial for application to new types of food packaging or for replacing environmentally persistent antiflammable compounds.

In addition to clay, carbon-based nanomaterials such as CNT or graphene are candidate nanocoatings to improve substrate flame-retardancies. Wu et al. tried using single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) as ~20 μm thick buckypapers to protect carbon-fiber-reinforced epoxy composites from fire [101]. Although the MWNT buckypaper was an effective flame-retardant shield, SWNT one was not. The MWNT buckypaper reduced the substrate PHRR by ~50 %; the SWNT one, on the other hand, reduced it by <10 %. The SWNT buckypaper effective air diffusivities were superior to the MWNT buckypaper ones owing to the dense SWNT network. However, unlike the MWNT buckypaper, the SWNT buckypaper could not improve the flame retardancy because SWNTs are less thermally stable than MWNTs. In fact, Wu et al. showed that the SWNT buckypaper had burned away during combustion, leaving only a red iron-catalyst residue. The MWNT buckypaper showed high thermal stability and had survived combustion. Liu et al. coated cotton fibers with CNTs and improved the fiber mechanical properties and flame retardancy [102]. They used simple dip-coating to fabricate CNT-network armors on the fiber surface and found that the CNT-coated cotton textiles exhibited enhanced mechanical properties and extraordinary flame retardancy because the CNTs had reinforced and protected the fibers.

Nanocoating technology drastically improves substrate flame retardancy. A thin nanomaterial coating can improve not only substrate fire retardancy but also substrate mechanical properties, gas permeability, and other functionalities such as UV-blocking. However, nanocoating technology must be further developed to improve long-term nanocoating reliability before applying nanocoatings to commercial products. Nanocoating flame-retardancy efficiency diminishes when nanocoatings develop cracks after long-term environment exposure because the main flame-retardancy mechanism involves nanocoatings acting as gas barriers, and cracks of nanolayer degrade the gas barrier property. However, nanocoatings can be powerful tools for improving polymer flame retardanciesy if these problems are solved.

2.5 Conclusions

This review has demonstrated polymer-nanocomposite flame retardancy toward replacing halogenated flame retardants with safe, eco-friendly polymer nanocomposite ones. Nanocomposites should be combined with proper flame retardants to achieve the same flame retardancies that halogenated compounds show. The main nanofiller flame-retardancy mechanism involves nanofillers acting as barriers against gas flow and oxygen diffusion at the condensed phase. Therefore, producing strong, dense, crack-free nanocoating surface layers during combustion is the key factor in producing effective polymer nanocomposite flame retardants. Nanofiller dispersion and distribution are important factors contributing to flame retardancy synergistic effects, which are unobtainable when nanofillers are incorporated into other flame retardants because poor nanofiller distribution scatters surface layers rendering them unable to act as barrier layers. Nanofiller/flame-retardant interactions also contribute to nanofiller flame-retardant efficiency. Dense char networks can form and the nanoreinforced char layers can act as barriers against heat propagation and gas diffusion when nanofillers interact with flame retardants. Combining flame retardants that interact during thermal degradation maximizes ternary-composite flame retardancy. Although nanocoating technology has the potential to minimize material flammabilities, it must be further developed to improve long-term nanocoating reliability before applying nanocoatings to commercial products. The enhanced nanofiller flame retardancies and improved mechanical, gas-barrier, etc. properties of polymer nanocomposite flame retardants may expedite the practical application of such nanocomposites.

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Chapter 3
Recent Developments in Different Techniques Used for the Flame Retardancy

Tao Xu

Abstract To improve the flame retardancy of polymer blends, composites and nanocomposites for extending their application, recent developments in different techniques used for the flame retardancy are reviewed in this chapter. We introduce the fundamentals of experimental methods such as cone calorimetry and UL 94 used to describe fire behavior. Also the pyrolysis process of condensed phrase is presented to prevent further pyrolysis of polymeric materials. Additionally, the combustion process of polymeric materials is described for selecting feasible flame retardants to reduce the amount of flammable volatiles emitted during combustion. At the same time, the smoke formation is discussed during fire for reduce smoke to protect environments and human's health. Finally, the future trends of different techniques utilized for the flame retardancy are introduced such as nanotechnology, catalysis reaction, vapor phase flame retardant and flame retardant synergy.

Keywords Polymer blends · Composites · Nanocomposites · Flame retardancy · Cone calorimetry · UL 94 · Condensed phase pyrolysis · Polymer combustion · Smoke formation

3.1 Introduction

The massive use of polymer blends, composites and nanocomposites is driven by their remarkable combination of properties, low weight and ease of processing. However, the use of organic polymeric materials is limited in many applications because of fire hazard [1]. Such materials are also known for their relatively high

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flammability; most often accompanied by the production of corrosive or toxic gases and smoke during combustion. Consequently, improving the fire retardant behavior of these materials is a major challenge for extending their use to most applications [2].

The widespread applications of polymer blends, composites and nanocomposites require the use of conventional flame retardants based on halogen and phosphorous compounds to satisfy fire safety regulatory standards. However, these compounds, particularly halogen-based examples, are persistent organic pollutants of global concern and generate corrosive and toxic combustion gaseous products [3].

Considering the eco-friendliness, safety requirements are currently becoming more and more drastic in terms of polymers' reaction to fire and their fire resistance performances, while various flame retardant additives, such as halogenated additives, are being phased out for their proven or suspected adverse effects on the environment. The combined challenge thus consists in developing effective and environmentally friendly flame retardant systems for above materials. Although the incorporation of non-toxic fillers in materials shows positive potential towards flame retardancy, many obstacles remain [4].

Additionally, combustion of polymeric materials is a complex process involving simultaneous combinations of heat, energy and mass transfer and diffusion, fluid dynamics and degradation chemistry. Some studies on the fire response of such materials are conducted from the perspectives of short-term and long-term fire exposure tests, theoretical modeling or numerical simulation. Also many techniques are used for the flame retardancy of such materials. Hence, there is a need to fundamentally understand the recent development in different techniques used for the flame retardancy [2].

Currently, the most common approach to improve the flame retardancy performance of materials is to add flame retardants, such as halogen-based agents, phosphorous-based compounds, metal hydroxides, intumescent agents, boron and nitrogen-based flame retardants, etc. [5]. Depending on the type and nature of flame retardants, they act chemically and/or physically in the solid, liquid or gas phases and interfere with combustion at different stages (heating, decomposition, ignition, or flame spread). The mechanisms of conventional flame retardants based on halogen, phosphorous and in tumescent compounds have been thoroughly discussed in the past [2].

Simultaneously, smoke suppressants are developed because the majority of human deaths during fire incidents are related to the inhalation of smoke and toxic combustion gases, with carbon monoxide being particularly significant. Some approaches that were adopted to tackle this problem include the use of fillers or additives, surface treatments, and chemical or physical modification. All these are to slow down the thermal decomposition of polymer blends, composites and nanocomposites and reduce the smoke density and gas concentration [3].

Recently, the polymer nanocomposite approach to flame retardancy is the newest technology now in use. Polymer nanocomposites are polymers filled with nanoscale particles finely dispersed in the polymer matrix [6–8]. For flame retardancy, polymer nanocomposites are condensed phase flame retardants that slow the mass loss rate of the polymer during fire conditions through formation of a nanoparticle-rich fire protection barrier [9]. This leads to a lowering of peak heat release rate and inhibition of polymer flow (melting/dripping) during a fire, but it does not lower the total heat release of the fuel; it just spreads it out over a longer time and makes it burn less intensely [10].

In addition, nanocomposites show earlier time to ignition as can be seen in but many other flame retardants show early time to ignition as well, so this effect may or may not be a negative feature [11]. More recently, it has been reported that the presence of nanodispersed particles in polymeric matrices produces a substantial improvement in fire performance [6].

The flammability of polymer materials can be characterized by their ignitability, flame-spread rate and heat release. There are numerous small-, intermediate- or full-scale flammability tests used in industrial or academic laboratories for either screening materials during product development or testing manufactured products, for instance, UL 94 and cone calorimetry.

To protect against fire, it is necessary to (a) understand the flame measurement such as cone calorimetry and UL 94; and (b) know the pyrolysis process of condensed phrase for preventing further pyrolysis of polymeric materials; or (c) describe the combustion process of polymeric materials for selecting feasible flame retardants to reduce the amount of flammable volatiles emitted; or (d) reduce the smoke formation during fire for protecting environments [12].

In this chapter, we present the fundamentals of tests used to describe fire behavior, condensed phrase pyrolysis, polymer combustion, smoke formation and new prospects in different techniques used for the flame retardancy of polymer blends, composites and nanocomposites.

3.2 Cone Calorimetry

The Cone Calorimeter test is at present the most advanced method for assessing materials reaction to fire. This name was derived from the shape of the truncated conical heater that is used to irradiate the test specimen with fluxes in the test. The test apparatus consists of the following components: a conical radiant electric heater; specimen holders; an exhaust gas system with oxygen monitoring and flow measuring instrumentation; an electric ignition spark plug; a data collection and analysis system; and a load cell for measuring specimen mass loss [13]. A photo of the apparatus is shown below. A photo of the apparatus is shown in Fig. 3.1.

The calorimeter is used by having a small sample encased in aluminum foil, wool, and a retainer frame that is ignited below an exhaust hood. A conical heater is placed in between in order for materials to combust. The cone-shaped apparatus outputs high amounts of energy and turns electricity into heat. Without this portion of the device, it would be very difficult to measure the temperature,

Fig. 3.1 A photo of cone calorimeter

pressure, and smoke coming off the sample. The conical heater is what makes this device different from the rest, but in reality is only a small part of the entire apparatus [14].

Ventilation is also a very important part of the device, as well as the electrical power to run the conical heater. A small water supply is necessary to cool and regulate the heat in the system of the device. Since temperature and pressure are being evaluated, two different measurement tools are needed in the exhaust tube. Gas samples, smoke measurements, and soot collections are also collected using this device and all need a place to be measured after the exhaust tube [14].

Also, the measurements of smoke and toxic gases can be conducted during this test. The test gives a possibility to evaluate ignitability, combustibility, production of smoke and toxic gases, etc. Recently, the cone calorimeter is a relatively developed to supply an integrated set of physical chemical parameters of the combustion. Currently, the cone calorimeter is the most significant bench scale instrument in the field of fire testing. The test schematic representation of cone calorimeter is shown in Fig. 3.2.

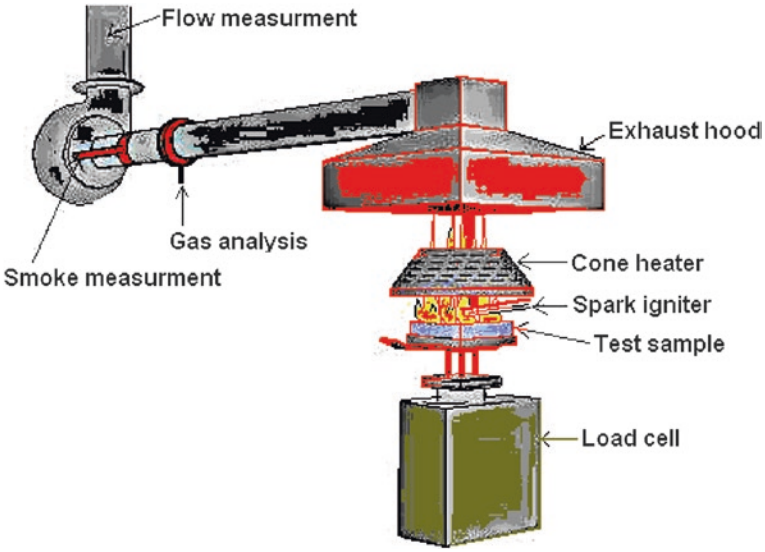

Fig. 3.2 Test schematic representation of cone calorimeter

3.2.1 Usage

Cone calorimeter is a modern device used to study the fire behavior of small samples of various materials in condensed phase. It is widely used in the field of fire safety engineering [15]. The cone calorimeter test has been developed for material fire evaluations, computer modeling, design purposes, and development and research to help make real world fire predictions. The test performance uses the bench-scale system to measure fire characteristics associated with heat and smoke output. The measurements can be used directly by researchers or can be used as data input into correlation or mathematical models used to predict fire development. The cone calorimeter became the premier dynamic research tool based on the principle of oxygen consumption calorimetry [15].

The data from the test results can be used for technical modeling bigger fires. The cone calorimeter test is also largely used when testing products that are under development. A whole range of different data can be compared in order to eliminate products that will not have the sufficient fire characteristics. In the test, Various output data are collected including peak rate and average rate of heat release, total heat released, effective heat of combustion, specific extinction area, exhaust flow rate, mass loss rate and final sample mass, time to sustained ignition, O_2, CO, CO_2, and toxic gas concentrations, and smoke density as a function of time. Heat release is the key measurement required to assess the fire development of materials and products; radiant heat is the major cause of fire spread and the cone measures intensity of the peak rate of heat release and the speed to reach the peak rate; the critical factors in predicting the growth rate of fire [14].

Cone testing can also be utilized by a product manufacturer who is looking to change a component within a product to a new material and wishes to investigate the effect, if any, that change would have on the product's fire safety. In these cases, testing the new component and the old component in the cone and comparing the thermal properties of the two can be performed in lieu of more expensive full-scale testing. Additionally, the Cone is used as a screening tool for new polymeric materials that are in the development. And the cone can compare the thermal properties of the materials and weed out the worst performers [16].

The different models of the calorimeter can be used to evaluate different aspects of the flammable materials. The research using the cone calorimeters can be used for product safety, environment, and health services. This device is important when dealing with safety issues. It is easier to see how many different materials react with fire using the device. Knowing that information, safety regulations can be made easily to protect the people that come in contact or work with the material often. It is important to know and understand the flammability, heat of combustion, ignitability, heat release, and smoke production of many materials in order to maintain a safe environment, all of which can be found by using a calorimeter [16].

In short, the cone calorimeter is an extremely useful in the department of fire safety and analytical services. The calorimeter is a unique apparatus that is able to study small samples of materials, in order to determine their flammability. The fire characteristics of the material can be determined from several different standard models of the cone calorimeter. A list of various test standards is provided such as ISO 5660, ASTM E1354, ASTM E1474, ASTM E1740, ASTM F1550, ASTM D6113, CAN ULC 135, and BS 476 Part 15 [15, 16].

3.2.2 Test Principle

Cone calorimetry is one of the most effective medium-sized polymer fire behavior tests. The principle of cone calorimeter experiments is based on the measurement of the decreasing oxygen concentration in the combustion gases of a sample subjected to a given heat flux. The surface of the test specimen is exposed to a constant level of heat irradiance, within the range 0–100 kW/m^2, from a conical heater (Fig. 3.3). Volatile gases from the heated specimen are ignited by an electrical spark igniter. Combustion gases are collected by an exhaust hood for further analysis. This gas analysis makes it possible to calculate heat release rate and to assess production of toxic gases from the specimen [16].

Also smoke production is assessed by measuring attenuation of a laser beam by smoke in the exhaust duct. The attenuation is related to volume flow, resulting in a measure of smoke density called smoke extinction area [m^2/s]. The specimen is mounted on a load cell which records the mass loss rate of the specimen during combustion. A thorough analysis requires testing at several irradiance levels. Typical levels of irradiance are 25, 35, 50 and 75 kW/m^2. Three specimens shall be tested at each heat flux level.

Fig. 3.3 A photo of conical heater

3.2.3 *Test Specimens*

The surface of the specimens shall be essentially flat. The specimens shall be representative of the product, and as far as possible be similar to the final product.
Dimensions of the specimens:
Area: 100 mm × 100 mm
Thickness: 50 mm

3.2.4 *Test Procedure*

A sample with the dimension 100 mm × 100 mm is subjected to a specific irradiance level. The surface of the sample is heated and starts to emit pyrolysis gases that ignite by a spark igniter. The emitted gases are collected in a hood and transported away through a ventilation system. The heat release is measured using the data on measured oxygen concentration in the emitted smoke. The smoke production is measured continually throughout the test with a laser system (See Fig. 3.2).

Device usually allows the test sample to be exposed to different heat fluxes over its surface. It gathers data regarding the ignition time, mass loss, combustion products, heat release rate and other parameters associated with its burning properties. The cone calorimeter introduced a system for measuring smoke optically and soot yield gravimetrically. It is now considered one of the most important devices for fire engineering and safety services, and its usage in research has grown increasingly over the years [16].

3.2.5 Test Report

The cone calorimeter test is very well suited to quantify materials reaction to fire. The test report contains information about dimensions, pretreatment and conditioning of the test specimens, and information about the test conditions. The test results can give information on how to improve the tested product. The following test results are tabulated:

Time to ignition [s]
Total heat released [MJ/m^2]
Maximum heat release rate [kW/m^2]
Average heat release rate after 180 s and after 300 s [kW/m^2]
Effective heat of combustion [MJ/kg]
Average smoke production [m^2/s]
Production of CO (carbon monoxide) [g]

3.3 UL 94

The UL 94 V test is widely used both in industry and academic research centers, and is intended to meet industrial requirements as well as to hierarchically classify the polymeric materials [17]. UL 94 intends this standard to serve as a preliminary indication of polymer acceptability for use as part of a device or appliance with respect to its flammability. It is not intended to reflect the hazards of a material under actual fire conditions. UL 94 flammability testing is the first step toward obtaining a plastic recognition and subsequent listing in the Plastics Recognized Component Directory [18].

UL 94 flame rating groups materials into categories based on their flammability. UL 94 covers two types of testing: vertical burn and horizontal burn. Vertical burn test includes Vertical Testing (V-0, V-1, V-2), Vertical Testing (5VA, 5VB) and Vertical Testing of Thin Materials (VTM-0, VTM-1, VTM-2). Specimens molded from the plastic material are oriented in either a horizontal or vertical position depending on the specifications of the relevant test method, and they are subjected to a defined flame ignition source for a specified period of time [18].

The set of UL 94 tests has been approved as tests of the flammability of plastic materials for parts in devices and appliances. It includes a range of flammability tests (small and large flame vertical tests, horizontal tests for bulk and foamed materials, radiant panel flame-spread test). In terms of practice and usage, the most commonly used test is UL 94 V for measuring the ignitability and flame-spread of vertical bulk materials exposed to a small flame [17].

3.3.1 Horizontal Testing (HB)

An HB flame rating indicates that the material was tested in a horizontal position and found to burn at a rate less than a specified maximum [19]. A specimen is

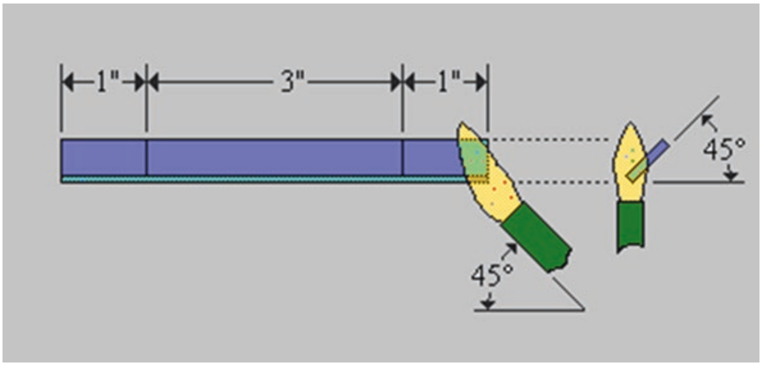

Fig. 3.4 Test schematic representation of horizontal testing

Table 3.1 Requirements of horizontal rating of horizontal testing

Horizontal rating	Requirements
HB	(1) Specimens must not have a burning rate greater than 1.5 in./min for thicknesses between 0.120 and 0.500 in. and 3 in./min for thicknesses less than 0.120 in.
	(2) Specimens must stop burning before the flame reaches the 4 in. mark

supported in a horizontal position and is tilted at 45°. A flame is applied to the end of the specimen for 30 s or until the flame reaches the 1 in. mark. If the specimen continues to burn after the removal of the flame, the time for the specimen to burn between the 1 and 4 in. marks are recorded. If the specimen stops burning before the flame spreads to the 4 in. mark, the time of combustion and damaged length between the two marks is recorded. Three specimens are tested for each thickness [19]. The test schematic representation of horizontal testing is shown in Fig. 3.4. Requirements of horizontal rating of horizontal testing are given in Table 3.1.

3.3.2 Vertical Testing (V-0, V-1, V-2)

A specimen is supported in a vertical position and a flame is applied to the bottom of the specimen [17]. The flame is applied for 10 s and then removed until flaming stops at which time the flame is reapplied for another 10 s and then removed. Two sets of five specimens are tested. The two sets are conditioned under different conditions. Test schematic representation of Vertical Testing (V-0, V-1, and V-2) is shown in Fig. 3.5. Requirements of vertical ratings of vertical Testing (V-0, V-1, and V-2) are given in Table 3.2.

The three vertical ratings, V0, V1 and V2, indicate that the material is tested in a vertical position and self-extinguished within a specified time after the ignition source is removed. The vertical ratings also indicate whether the test specimen

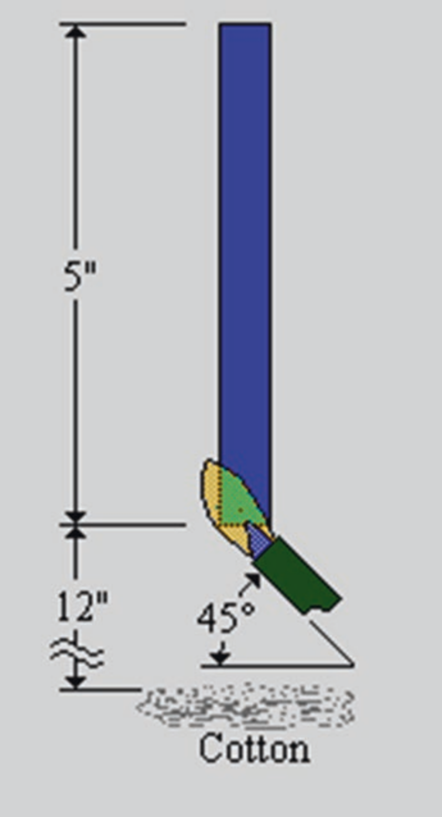

Fig. 3.5 Test schematic representation of vertical testing (V-0, V-1, V-2)

dripped flaming particles that ignited a cotton indicator located below the sample. These small-scale tests measure the propensity of a material to extinguish or spread flames once it becomes ignited.

3.3.3 Vertical Testing (5VA, 5VB)

UL 94 also describes a method in which the test flame is applied for up to five applications in testing for a 5VA or 5VB classification [18]. Testing is done on both bar and plaque specimens. A bar specimen is supported in a vertical position and a flame is applied to one of the lower corners of the specimen at a 20° angle. The flame is applied for 5 s and is removed for 5 s. The flame application and removal is repeated five times. However the procedure for plaques is the same as for bars except that the plaque specimen is mounted horizontally and a flame is applied to the center of the lower surface of the plaque. Test schematic representation of vertical testing (5VA, 5VB) is shown in Fig. 3.6. Requirements of vertical ratings of vertical testing (5VA, 5VB) are given in Table 3.3.

Table 3.2 Requirements of vertical ratings of vertical ratings (V-0, V-1, V-2)

Vertical ratings	Requirements
V-0	(1) Specimens must not burn with flaming combustion for more than 10 s after either test flame application
	(2) Total flaming combustion time must not exceed 50 s for each set of 5 specimens
	(3) Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	(4) Specimens must not drip flaming particles that ignite the cotton
	(5) No specimen can have glowing combustion remain for longer than 30 s after removal of the test flame
V-1	(1) Specimens must not burn with flaming combustion for more than 30 s after either test flame application
	(2) Total flaming combustion time must not exceed 250 s for each set of 5 specimens
	(3) Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	(4) Specimens must not drip flaming particles that ignite the cotton
	(5) No specimen can have glowing combustion remain for longer than 60 s after removal of the test flame
V-2	(1) Specimens must not burn with flaming combustion for more than 30 s after either test flame application
	(2) Total flaming combustion time must not exceed 250 s for each set of 5 specimens
	(3) Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	(4) Specimens can drip flaming particles that ignite the cotton
	(5) No specimen can have glowing combustion remain for longer than 60 s after removal of the test flame

3.3.4 Vertical Testing (VTM-0, VTM-1, VTM-2)

This test is used for materials that are thin, or are too flexible or may distort, shrink or flex during ordinary vertical testing [20]. An 8 in. × 2 in. specimen is rolled longitudinally around a 1/2 in. diameter mandrel and taped on one end. When the mandrel is removed the specimen forms a cone. The cone is supported in a vertical position and a flame is applied to the bottom of the specimen. The flame is applied for 3 s and then removed until flaming stops at which time the flame is reapplied for another 3 s and then removed. Two sets of five specimens are tested. The two sets are conditioned under different conditions [20]. Test schematic representation of vertical testing (VTM-0, VTM-1, and VTM-2) is shown in Fig. 3.7. Requirements of vertical ratings of vertical testing (VTM-0, VTM-1, and VTM-2) are given in Table 3.4.

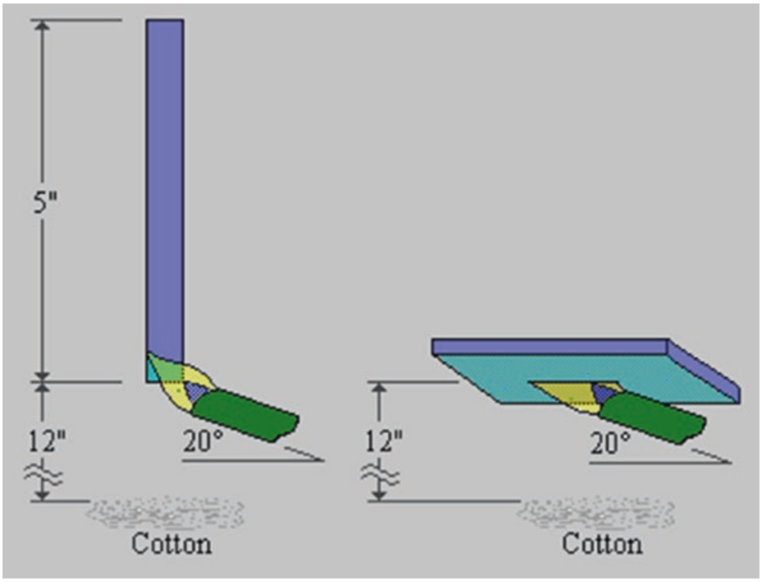

Fig. 3.6 Test schematic representation of vertical testing (5VA, 5VB)

Table 3.3 Requirements of vertical ratings of vertical testing (5VA, 5VB)

Vertical ratings	Requirements
5VA	(1) Specimens must hot have any flaming or glowing combustion for more than 60 s after the five flame applications
	(2) Specimens must not drip flaming particles that ignite the cotton
	(3) Plaque specimens must not exhibit burn through (a hole)
5VB	(1) Specimens must hot have any flaming or glowing combustion for more than 60 s after the five flame applications
	(2) Specimens must not drip flaming particles that ignite the cotton
	(3) Plaque specimens may exhibit burn through (a hole)

Some differences between cone calorimetry and UL 94 will be highlighted below:

(1) Cone calorimeter evaluates the material response to a constant heat flux with time (forced combustion), whereas in UL 94, the response of a material to a removed fire and its self-extinguishing behavior versus time are measured. That is, UL 94 provides information in a local ignition fire scenario, but their safety level is not so clear when exposed to a more aggressive fire scenario [21]. Moreover, the test operator has to follow the polymer with the Bunsen burner flame during the test, and therefore, maintaining a steady ignition source on a moving/curling/dripping thermoplastic is difficult [22]. This obviously induces fluctuations and a degree of uncertainty in the UL 94 test data.

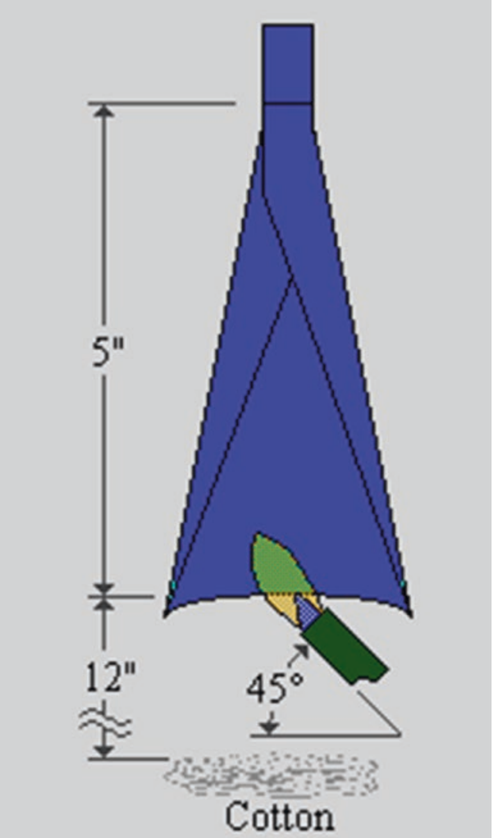

Fig. 3.7 Test schematic representation of vertical testing (VTM-0, VTM-1, VTM-2)

Table 3.4 Requirements of vertical ratings of vertical testing (VTM-0, VTM-1, VTM-2)

Vertical ratings	Requirements
VTM-0	(1) Specimens must not burn with flaming combustion for more than 10 s after either test flame application
	(2) Total flaming combustion time must not exceed 50 s for each set of 5 specimens
	(3) Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	(4) Specimens must not drip flaming particles that ignite the cotton
	(5) No specimen can have glowing combustion remain for longer than 30 s after removal of the test flame
	(6) No specimen shall have flaming or glowing combustion up to a mark 5 in. from the bottom of the specimen

(continued)

Table 3.4 (continued)

Vertical ratings	Requirements
VTM-1	(1) Specimens must not burn with flaming combustion for more than 30 s after either test flame application
	(2) Total flaming combustion time must not exceed 250 s for each set of 5 specimens
	(3) Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	(4) Specimens must not drip flaming particles that ignite the cotton
	(5) No specimen can have glowing combustion remain for longer than 60 s after removal of the test flame
	(6) No specimen shall have flaming or glowing combustion up to a mark 5 in. from the bottom of the specimen
VTM-2	(1) Specimens must not burn with flaming combustion for more than 30 s after either test flame application
	(2) Total flaming combustion time must not exceed 250 s for each set of 5 specimens
	(3) Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	(4) Specimens can drip flaming particles that ignite the cotton
	(5) No specimen can have glowing combustion remain for longer than 60 s after removal of the test flame
	(6) No specimen shall have flaming or glowing combustion up to a mark 5 in. from the bottom of the specimen

(2) Horizontal versus vertical configuration—another parameter that is highly relevant is the horizontal (cone calorimeter) versus vertical (V-UL 94) configuration; this is particularly important for injection a molded polymers with 2D nanofillers. The differences in the orientation of clay layers will affect the fire performance of the sample. Moreover, in the vertical configuration, dripping should be considered; while in cone calorimeter, the bottom of the material is securely wrapped in an Al-foil.

3.4 Condensed Phase Pyrolysis

Pyrolysis of polymeric materials is a complex process involving simultaneous combinations of heat, energy and mass transfer and diffusion, fluid dynamics and degradation chemistry [23]. The study on polymer combustion and fire retardancy is a complex multidisciplinary topic, encompassing physical and chemical phenomena occurring in the gas and condensed phase. Thus, aspects involved are physical chemistry of flames and thermal degradation of polymers, respectively [24].

The processes occurring in the condensed phase are of primary importance because they originate the volatile species which feed the flame. Techniques and methods of general use in the study of thermal degradation of polymers are applied to the study of condensed phase processes in combustion and fire retardancy [25].

However, thermal degradation of polymers may strongly depend on experimental conditions such as temperature, type of atmosphere, rate of heating, pressure, etc. In order to obtain basic information which is relevant to the understanding of the combustion process, the thermal degradation must be carried out in conditions simulating those to which the polymer is exposed during combustion [25].

Combustion of synthetic polymer materials is characterized by a complex coupling between condensed and gas phase phenomena. Furthermore, the phenomena in each phase consist of a complex coupling of chemical reactions with heat and mass transfer processes. Since the gas phase phenomena, such as chemical reaction, turbulence, soot formation, and so on, have been extensively studied and described elsewhere, this section concentrates on the less-explored condensed phase phenomena [26]. Generally combustion of polymers is a gas-phase process with gaseous fuel supplied by the decomposing solid or liquid polymer. Thus, understanding of polymer pyrolysis is important to understanding the chemistry and physics of polymer combustion and flammability.

3.4.1 Heat Transfer

When polymer is exposed to heat such as a source of ignition, or the combustion flame, the surface temperature of the polymer can rise to a point at which its structure will break down and it will release volatile material [27]. Therefore the polymer behavior in a fire risk situation is the result of a combination of many different physical and chemical processes, which happen in the condensed phase. The kinetics of these processes are particularly important both as a function of temperature and relative to each other. Physical properties are thermal conductivity, heat capacity and the ability to melt back away from an ignition source. As part of the degradation mechanism some polymers will also produce carbonaceous char [27].

The temperature of the solid polymer is raised either due to an external heat source such as radiation or a flame, or by thermal feedback. During the initial exposure to heat thermoplastics, which have a linear chain structure, soften or melt and start to flow. On the other hand, thermosetting plastics have a three-dimensional cross-linked molecular structure which prevents softening or melting. Additional heat causes both types of polymer to pyrolyse and to evolve smaller volatile molecular species. Because of their structure this occurs at higher temperatures for thermosetting as opposed to thermoplastic polymers [28].

Also flame propagation is affected by physical factors, more specifically thermal transfers. Conductive and convective transfers are important in the initial phase of fire development when the height of the flame remains limited to a few tens of centimeters. In a more advanced phase, flame propagation on the surface contributes to a rapid increase in radiative transfer.

3.4.2 Energy Transfer

Pyrolysis is an endothermic process which requires the input of sufficient energy to satisfy the dissociation energies of any bonds to be broken plus any activation energy requirements of the process [29]. In order to burn a polymeric material, thermal energy must be added to the material to raise its temperature sufficiently to initiate degradation. When temperatures near the surface become high, thermal degradation reactions occur and evolve small gaseous degradation products. The majority of the evolved products are combustible. Depending on the nature of the polymer, thermal degradation reactions may proceed by various paths.

The combustion process of polymers is a complex coupling of energy feedback from a flame to the polymer surface with gasification of the polymer to generate combustible degradation products. Combustion is a catalytic exothermic reaction maintained by internally generated free radicals and heat. Provided the supply of radicals and heat exceeds the energy required for combustion, the combustion proceeds at an increasing rate until an explosion occurs [30].

If the energy supply is constant and equals the demand, a stationary equilibrium will be established, i.e. a steady flame occurs. If the available energy is below that required to maintain this equilibrium, the rate of combustion will decrease until the flame extinguishes. The radicals, oxygen and heat necessary to sustain the combustion reach the site by various transport mechanisms.

Combustion reactions liberate the energy stored in the chemical bonds of the molecules of the polymer. A polymer is any substance that will release energy during its reaction with oxygen, usually in air, generally initiated by an external heat source. Thermal decomposition of a polymer is often initiated by dissociation of covalent bonds to form radicals. Bond dissociation energies will depend on the nature of the atoms making up the bond and also the precise structural environment in which the bond occurs [30].

Bond dissociation values can often be used to explain why one bond dissociates in preference to another, and are of particular importance for polymers, which degrade by free radical mechanisms. The mechanisms of polymer degradation and the temperatures at which they occur will depend very much on the polymer's structure. Polymers at their degradation temperature can form radicals due to bond scission.

3.4.3 Mass Transport

Development of new fire-safe polymeric materials requires a better understanding of the microscopic chemical processes that determine thermal stability and flammability of polymers [31]. As described above, the type of polymer structure, thermal properties, and the amount of heat transferred to the polymer determine the depth over which the polymer is heated sufficiently to degrade. Since the boiling temperatures of some of the degradation products are much less than the polymer degradation temperatures, these products are superheated as they form. They nucleate and form bubbles.

Then, these bubbles grow with the supply of more small degradation products to the bubbles by diffusion from the surrounding molten polymer. Since the polymer temperature is higher near the surface than further below, the polymer sample is more degraded there, and its molecular weight is lower. The net result is a highly complex generation and transport of bubbles containing small molecules from the interior of the polymer melt outward through a strong viscosity gradient that heavily influences bubble behavior [32].

During polymer thermal decomposition, the development of considerable material heterogeneity can be highlighted. A gradient structure tends to form inside the material, arising from the interaction with atmospheric oxygen, coupled with the out-diffusion of reactive species and also concomitant polymer chain breakdown within the material. Several zones inside the material can therefore be identified [33].

The gaseous decomposition products tend firstly to be located in the cavities of this underlayer, and afterwards migrate (through this microporous underlayer) towards the surface, where combustion takes place. The cellular under layer is in direct contact with the thermal decomposition zone of the polymer and lies on the top of another layer in which the polymer remains intact even if it may undergo phase transitions [33]. A schematic representation of thermal decomposition of polymeric materials is present in Fig. 3.8.

At present, it is clear that the subsurface degradation is important for the gasification, but it is not clear what the main transport process for the small degradation products to the sample surface is and also how rapid this transport is. It appears that diffusion of small molecule gases through a polymer is too slow to be responsible for the transport of the products.

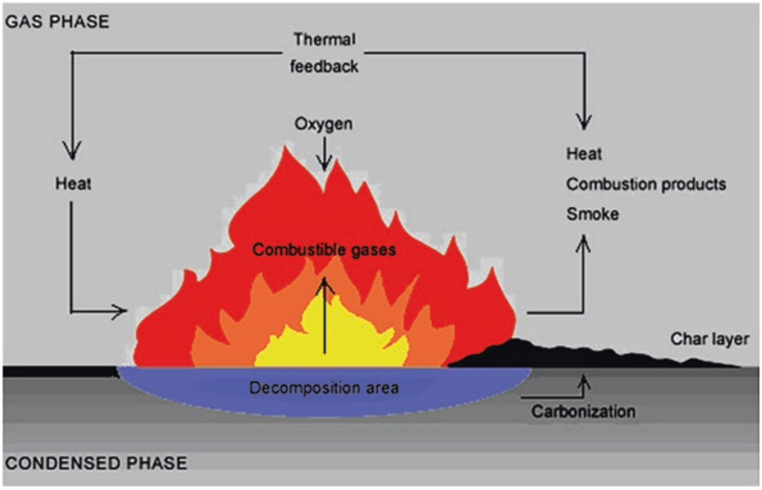

Fig. 3.8 A schematic representation of thermal decomposition of polymeric materials

3.4.4 Char Formation

Char formation during polymer degradation is generally a complex process and may involve several steps, including chemical fragmentation, conjugated double bond formation, cyclization, aromatization, fusion of aromatic rings, turbostratic char construction and graphitization [34].

Char formation is probably the most important condensed-phase mechanism for modifying the combustion process. It serves as a barrier to heat and mass flow, and as a means of stabilizing carbon, thus preventing its conversion to combustible gases. The efficiency of a char as a barrier in these processes depends greatly on its chemical and physical structure. The ability of char formation to prevent sustained ignition will also depend on its rate of formation in relation to other degradation mechanisms, especially the release of combustible gases. Polymers such as polycarbonate, novolaks and polyphenylene oxide all burn with the formation of a carbon rich residue called char. This char forming property is also reflected during thermogravimetric experiments which show initial degradation producing a more thermally stable material [34].

Char formation rate is important towards flame retardancy or flammability [35]. Phosphorus-based flame retardants can effectively result in char formation in oxygen- or nitrogen-containing polymers. In the absence of reactive groups, polyols like pentaerythritol, mannitol or sorbitol were used as char formers, particularly in intumescent formulations. Boron compounds, another topic mentioned in the preceding, promotes char formation in the burning process.

The mechanism is related to the thermal action of boric acid with alcohol moieties. Addition of dehydrogenation or oxidative dehydrogenation catalysts is another interesting possibility, not yet explored. This is based on the concept that the heat of combustion of a reaction consuming only hydrogen of an aliphatic hydrocarbon polymer molecule is only about one-third that of both hydrogen and carbon [36]. When temperatures near the polymer surface become high, thermal degradation reactions occur and evolve small gaseous degradation products. The majority of the evolved products are combustible. Depending on the nature of the polymer, thermal degradation reactions may proceed by various paths.

Char-forming thermoplastics often swell and intumesce during their degradation/combustion, and one recent flame-retardant approach is to promote the formation of such intumescent char. Degradation of a polymer is often affected by the presence of abnormal structures that are usually less thermally stable than the regular structures. Some such structures are inherent consequences of the method of polymerization. If a vinyl polymer is polymerized with a free radical initiator, termination reactions yield unsaturated end groups and also a head to head linkage within the chain. These abnormal structures were found in PMMA, and it was shown that they lowered the thermal stability of the polymer and reduced ignition delay time and increased burning rate [36].

3.4.5 Char Structure

Char is a highly cross-linked, porous solid and consists of disordered polycyclic aromatic hydrocarbons that become more ordered with increasing temperature (lower amorphous concentration and higher aromaticity). Nevertheless, char formation during combustion is always beneficial whether this points to the materials that are unburned (therefore, not contributing to heat release) or to a higher fire retardancy by serving as a barrier to heat and mass transfer [36].

The char structure is conjugated multiple bonds, transition from a linear to a cross-linked structure, and an increase in the aromaticity of the polymer residue. For polymers containing aromatic carbon and/or heterocyclic links in the main chain of the polymer structure, general features of their pyrolysis and char yield have been derived. Some features are as follows: (1) the thermal stability and the char yield increase with the relative number of aromatic groups in the main chain per repeat unit of the polymer chain; (2) the thermal stability of heterocyclic polymers increases with the aromatic component of the heterocycles; and (3) pyrolysis begins with the scission of the weakest bonds in the bridging groups connecting the aromatic rings or heterocycles [35, 36].

The degree of protection provided by a char during combustion depends on both its chemical and physical structure. Whereas pure graphite is highly stable to heat and oxygen, chars from polymer combustion do not have this property. Although chars are richer in carbon than the original polymer, they are rarely all carbon. The ideal char for fire retardant properties is an intact structure of closed cells containing pockets of gas. For this to happen the bubbles of gas must become frozen into the expanding and thickening polymer melt, which ultimately solidifies to produce the honeycombed structure. This prevents the flow of volatile liquids or vapours into the flame and provides sufficient thermal gradient to keep the remaining polymer or polymer melt below its decomposition temperature [36].

3.5 Polymer Combustion

3.5.1 Combustion Process

Combustion and flammability of polymeric materials are important topics of practical interest directly related to fire safety [37]. Polymer combustion is a complex process involving a multitude of steps and is best described in qualitative terms. In general, four major steps comprise polymer combustion: ignition, pyrolysis, combustion and feedback [38]. Depending on the flammability limit of the material, ignition is normally caused by the presence of an external heat source such as a flame or a spark or, if the temperature is high enough, occurs spontaneously.

Organic polymers can initiate or propagate fires because they undergo thermal degradation to volatile combustible products. If the concentration of the degradation products in the air is within flammability limits, they can ignite either spontaneously, if their temperature is large enough, or by effect of an ignition source such as a spark or a flame. The combustion process continues then to complete consumption of the material, if the heat fed back from the flame to the polymer is sufficient to keep its rate of degradation above the minimum value for feeding the flame itself. Otherwise, the cyclic combustion process stops and the flame extinguish [39].

A self-sustaining combustion cycle will be formed after ignition if the heat evolved by the flame is sufficient to keep the decomposition rate of the polymer above that required to maintain the concentration of the combustible volatiles [40]. The duration of combustion cycle depends on the quantity of heat liberated during the combustion. When the amount of heat liberated reaches a certain level, new decomposition reactions are induced in the solid phase, and therefore more combustibles are produced. The combustion cycle is thus maintained as shown in Fig. 3.9.

In fact, combustion of polymeric materials involves simultaneous combinations of heat and mass transfer or diffusion, fluid dynamics and degradation chemistry. The whole combustion process usually starts with an increase in the temperature of the polymeric materials due to a heat source, to such an extent that it induces polymer bond scissions. The heat can be derived by a contribution of thermal energy from an external heat source (radiation, convection or conduction), by a chemical process induced inside the material or by the exothermicity of the combustion reaction initiated. The increase in temperature depends primarily on the heat flow, and the difference in temperature due to the exothermicity of the reactions involved, and the specific heat and thermal conductivity of the polymeric materials [41].

In the presence of a source of sufficient heat (to induce bond scissions), polymers will decompose or pyrolyze evolving flammable volatiles [38]. The exact physics and chemistries that occur in polymer combustion are dictated by the polymer that is burning. The chemical structure of the polymer and how it behaves

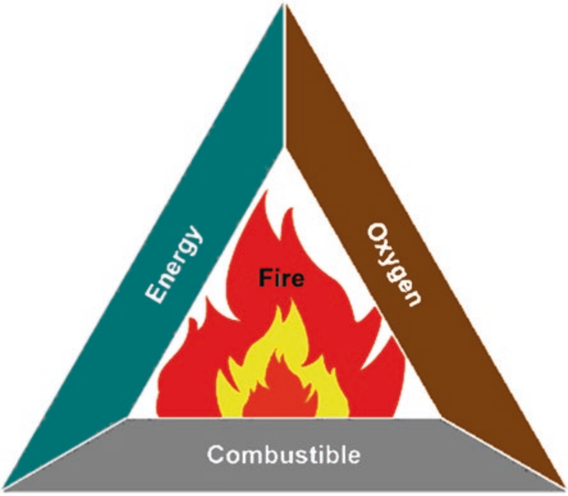

Fig. 3.9 A fire triangle of polymeric material combustion

upon exposure to heat will determine how much heat, smoke, and other gases are released when that polymer burns. In addition, the combustion behavior of polymeric materials is not an intrinsic property depending solely on its chemical structure. In fact, the behavior of the material depends as well on extrinsic factors such as heat irradiance, ventilation, shape, size and density of the specimen, etc.

3.5.2 Products of Combustion

Polymeric materials are made up mainly of carbon and hydrogen which causes such materials to be highly combustible. Polymer combustion is driven by the thermally induced decomposition (pyrolysis) of solid polymer into smaller fragments, which then volatilize, mix with oxygen, and combust. This combustion releases more heat, which reradiates onto the unburned polymer, thus continuing to drive pyrolysis and combustion until a lack of heat/fuel/oxygen causes the fire to extinguish. This is admittedly a simplistic explanation, but it holds basically true for just about all polymeric materials [42].

Thermoplastic polymers have a tendency to drip and flow under fire conditions, which can lead to additional mechanisms of flame spread or propagation whereas thermoset polymers tend to not drip and flow and instead produce pyrolysis gases from the surface of the sample directly into the condensed phase. The volatile fraction of the resulting polymer fragments diffuses into the air and creates a combustible gaseous mixture. This gaseous mixture ignites when the auto-ignition temperature is reached, liberating heat. Alternatively, the combustible volatiles can also ignite at a lower temperature upon reaction with an external source of intense energy [43].

3.5.3 Combustion Mechanism of Polymer

The combustion mechanism of polymer materials highly depends on the weakest bonds, and also on the presence or absence of oxygen in the solid and gas phases. Generally, thermal decomposition is the result of a combination of the effects of heat and oxygen [44]. They combine with air (oxygen) and produce the H_2–O_2 scheme, which propagates the fuel combustion by the branching reaction below:

$$H^\bullet + O_2 \rightarrow OH^\bullet + O^\bullet \tag{3.1}$$

$$O^\bullet + H_2 \rightarrow OH^\bullet + H^\bullet \tag{3.2}$$

The main exothermic reaction that provides most of the energy to maintain the flame is:

$$OH^\bullet + CO \rightarrow CO2 + H^\bullet \tag{3.3}$$

In oxidizing thermal conditions, the polymer reacts with oxygen in the air and generates a variety of low molecular weight products: carboxylic acids, alcohols, ketones, aldehydes, etc. Oxidation can lead to crosslinking through recombination reactions of the macromolecular radicals. The propagation rate of the degradation process is controlled by the wrenching reaction of hydrogen atoms from the polymer chains. The oxidation stability of the polymer thus depends on the C–H bond energy [44].

However, non-oxidizing thermal degradation is generally initiated by chain scissions under the simple effect of temperature (pyrolysis). This scission involves varying degrees of material depolymerization. Researchers [45] suggested that at combustion temperatures above 300 °C polymer degradation takes place via non-oxidizing thermal decomposition. Under these conditions, the rate of pyrolysis is much faster than the diffusion of oxygen in the solid phase. Oxidation therefore only occurs in the gas phase due to the presence of low molecular weight compounds produced by thermal decomposition.

The decomposition gases generated by pyrolysis first mix with oxygen by both convection and diffusion into the layer close to the surface, create free radicals, and then ignite. This ignition can be triggered by an external flame (flash ignition) or self-induced (self-ignition) when the temperature is sufficiently high. Ignition depends on several parameters, in particular oxygen concentration. The combustion of the gases increases the polymer temperature and thus supports the pyrolysis and production of new combustible gases. Combustion thus continues even in the absence of an external heat source.

3.5.4 Flame Retardancy Approaches

The fire safety of materials can be enhanced by increased ignition resistance, reduced flame spread rates, lesser heat release rates, and reduced amounts of toxic and smoke products, preferably simultaneously. When considering how to flame retard a polymeric material or protect that same material from a fire, there are three main approaches one can take. These are: engineering approaches, use of inherently low flammable polymers, and flame retardant additives [46].

The first approach, fire safety through an engineering approach, is one of the cheapest to implement. It is a solution, which seeks to find a way to get the polymer out of the fire risk scenario. This can be done with a fire protection shield or changing how the construction of the entire product is used such that it is removed from the fire risk scenario completely. However, the approach is easily implemented and often much cost effective, can be easily defeated [46].

The second approach is to use the polymeric materials with low heat release in a wide range of fire risk scenarios. This tends to be a rather robust method of fire protection, as it does not matter what the fire risk scenario is. Low heat release polymers can be fabricated into a wide range of forms, making them relatively easy to implement in a wide range of applications. However, these same low flammability polymers come with a high cost, and so their use can be limited for economic reasons [47].

The third solution is the addition of flame retardant additives in polymeric materials. The most common approach to enhance fire safety performance is the use of flame retardant additives to inexpensive polymers. The additives must have a minimum impact on physical properties and product cost. Although halogenated flame retardants are highly effective for reducing the heat release rate of commodity polymers, the future use of these retardants faces some questions. The environmental impact of the processing and combustion of certain halogenated flame retardants has become an issue. Flame retardant additives are used to limit the risk of fire and its propagation. They are incorporated in the polymer matrix to increase the time to ignition, improve the self-extinguishing ability of the polymer, decrease the heat release rate during combustion and prevent the formation of flammable drops.

This approach tends to be very cost effective, and is relatively easy to incorporate into a polymer. However, the use of flame retardant additives has its own problems, including potential for leaching into the environment, difficulty with recycling, and often a compromise in reaching a balance in the properties of the polymer [48]. There are six general classes of flame retardant such as halogenated flame retardants, phosphorus-based flame retardants, mineral filler flame retardants, intumescent flame retardants, inorganic flame retardants, and polymer nano-composites. All types of flame retardant chemistries fall into one (or more) of three mechanisms of flame retardant action [48].

(1) Gas phase flame retardants (ex. halogen, phosphorus)

    These materials reduce the heat released in the gas phase from combustion by scavenging reactive free radicals.

(2) Endothermic flame retardants (ex. metal hydroxides, carbonates)

    These materials function in the gas phase and condensed phase by releasing non-flammable gases (H_2O, CO2), which dilute the fuel and cool the polymer through endothermic decomposition of the flame retardant additive.

(3) Char-forming flame retardants (ex. intumescents, nanocomposites)

    These materials operate in the condensed phase by preventing fuel release through binding up fuel as non-pyrolyzable carbon (char) and providing thermal insulation for underlying polymer through the formation of char protection layers.

    It should be pointed out here that a flame retardant is a chemical applied for a particular application. It is not any different than a chemical applied for curing a disease (a pharmaceutical) or a chemical applied to provide color to a fabric (a pigment). What makes it different than pharmaceutical or pigment chemicals is that its sole purpose is to minimize the flammability.

3.6 Smoke Formation

3.6.1 Smoke Generation

The combustion of polymers involves a variety of processes (both physical and chemical) occurring in several phases. Thus, polymer melting and degradation, heat transfer in both solid and liquid phases and diffusion of the breakdown products through the degrading polymer into the gas phase accompany the various combustion reactions which occur. Polymers with aliphatic backbones, or those that is largely aliphatic and oxygenated, have a tendency toward low smoke generation, while polyenic polymers and those with pendant aromatic groups generally produce more smoke [49].

In the presence of a sufficiently intense heat source a polymer will pyrolyse, breaking down to low molecular weight species. These species diffuse from the solid phase into the gas phase, where they form the smoke observed in the absence of flame. At high heating rates and with ignition, these low molecular weight species fuel the polymer flame. The nature of the cracked species and pyrolyzates generated is thus a major factor in determining smoke formation, given similar conditions of polymer combustion [49].

The relative distribution of pyrolysis products from an individual polymer is dependent on the pyrolysis temperature, the heating rate and the pyrolysis atmosphere. The amount of smoke generated in a nitrogen atmosphere passes through maxima with increasing temperature in several of the polyesters whereas from others the smoke increases steadily with temperature. The structure of a polymer influences both flammability and smoke formation [50].

Visible smoke from burning polymers is generally a result of incomplete combustion. Within a flame, unsaturated hydrocarbon molecules formed by thermal cracking of the fuel will polymerise and dehydrogenate to form carbon, or soot. During these processes, intermediate molecules can form unsaturated species or they can cyclize to form polybenzenoid structures, both of which will lead to soot formation. These polybenzenoid structures take on more importance as intermediates when they are formed directly from aromatic fuels [50].

3.6.2 Smoke Toxicity

The majority of human deaths during fire incidents are related to the inhalation of smoke and toxic combustion gases, with carbon monoxide being particularly significant. It prevents oxygen transport by the formation of carboxyhemoglobin. By comparisons, though carbon dioxide released quantities during combustion of a polymer, is not specifically toxic, its presence in blood stimulates hyper-ventilation, increasing the respiration rate and thus making humans susceptible to the toxic components of the fire gases [51].

Flame retardants working through flame inhibition result in significantly increased smoke yields in the combustion. Both CO production and smoke production result from incomplete combustion. CO production and smoke production are strongly dependent on the material, and also on fire scenario [52].

Irrespective of the functionality of various organic/inorganic additives/fillers, the smoke produced, during burning of polymer materials, is always a mixture of toxic combustion gases along with a suspension of fine particles (mostly inorganic) and soot in the range of nanometers to micrometers, depending on the system. This is a particularly dangerous situation for fire-fighters and incident investigation teams.

3.6.3 Smoke Suppressant

Some of the approaches that were adopted to tackle smoke problem include the use of fillers/additives, surface treatments, and structural modification of the polymers themselves [53]. The idea behind the incorporation of fillers/additives (or conventional flame retardants), as discussed above is to slow down the thermal decomposition of the polymeric material and reduce the smoke density and gas concentration [54].

Polymers and polymer formulations can be modified so that additive smoke suppressing compounds are effective in reducing smoke during burning. Several of the smoke suppressant additives known to be effective in burner fuels are also effective in polymers. Approaches used for reducing smoke during burning have included the use of fillers, additives, surface treatments, and structural modification of the polymers themselves. Certain chemical reactions occurring during combustion processes affect the generation of visible smoke [55].

It is important to realize that polymer decomposition chemistry is very important when trying to address the fire hazard of a polymer through flame retardant approaches. When considering fire protection approaches, one must look at all aspects of the burning polymer: heat release, smoke release, mechanical integrity under fire conditions (such as flow or softening), and how that polymer behaves in a particular fire risk scenario [56].

Based on the functionality of smoke suppressant, fillers are categorized as inert and active. Inert fillers mainly act by diluting the amount of combustible material and to a smaller extent by absorbing heat to reduce the burning rate. While active fillers also promote the dilution process and heat absorption, they absorb more heat per unit weight by endothermic processes. Examples of inert fillers are silica, clays, calcium carbonate; metal hydroxides and oxides are a major class of active fillers. It has been proved that most metal compounds, in particular transition metal compounds such as copper, molybdenum and iron compounds, are the most effective smoke suppressants [55].

3.7 Future Trends

3.7.1 Nanotechnology

The interactions among various entities of the eco-system are highly complex between the environment and humans are multi-faceted. Considering eco-friendliness, the ultimate mechanical or physical properties required for end applications, and processing difficulties, the flame retardant option becomes too narrow. To obtain better flame, smoke and toxicity performance, emphasis is laid on using various nanoparticles as flame retardants, particularly high aspect ratio fillers. Even at low loadings with no additional flame retardants in the system, the flame retardancy of polymeric materials are greatly improved, in addition to huge delay in burning compared to corresponding neat polymers [57].

Despite this, there are many other problems with these materials, such as the total heat released during flame testing, inability to meet existing requirements of the ignition resistance tests, etc. Additionally, only qualitative terms are used to describe the observed phenomena, with little attention focused on quantitative and physical understanding. This obviously has resulted in conflicting or misleading suggestions on the applicability of materials from the perspectives of short-and long-term fire exposure tests [58].

The revolutionary development of chemical/polymer technology and nano-sciences over the past few decades have added to the seriousness of the issue with many direct and indirect effects including waste control and waste management. Recently many flame-retardants, such as bromine, commonly found in polymer blends, composites and nanocomposites are being replaced by other chemicals due to health and environmental risks associated with some brominated flame-retardants.

The analyses of flame retardancy behavior of polymer nanocomposites from the perception of the aforementioned issues will shed light on the use of conventional and potentially harmful flame retardants, and lay the foundation to promote the adoption of “green” and “environmentally benign” materials. It is believed that the polymer nanocomposites, i.e. polymer matrices filled with specific, finely dispersed nanofillers, will undoubtedly pave the way for future materials combining physicochemical and thermo-mechanical performances with enhanced flame retardant behavior.

Additionally, carbon nanotubes are an interesting alternative to the use of conventional flame retardants. The incorporation at low loading rate (<3 wt%) has been reported to improve the flammability of a large range of polymers. Carbon nanotubes display exceptional properties that can potentially be used in many applications ranging from macroscopic material composites down to nanodevices. Thanks to their high aspect ratio, carbon nanotubes percolate to form a network at very low loading in the polymer matrix and lead to substantial enhancement of several functional properties such as mechanical, rheological and flame retardant properties [59].

3.7.2 Catalysis Technique

One possible new area of flame retardant chemistry would be catalysis. Some transition metals at elevated temperatures can form more thermally stable carbon/carbon bonds and so the use of a catalyst to cause a polymer to crosslink and form a more thermally stable char, rather than break apart into smaller monomer pieces may be a promising new direction. There are already some studies out there showing that this technology may have promise, including the use of specific metal complexes [60], nanoscale metal oxides [61], and waste catalysts from olefin crackers [62], which help improve char formation and lower the flammability of the polymer.

3.7.3 Ceramic/Glass Shield

Another area of new flame retardant chemistry would be using ceramic/glass precursors, which melt under fire conditions to form a protective ceramic/glass shield on the top of the burning polymer. Obviously, because glasses and ceramics are already in their highest oxidation state, they cannot be burned further and so if successfully implemented would provide very robust fire safety to a polymeric material. The key to making this technology successful though is to get these inorganic precursors to fuse together at low temperatures (<400 °C) so that they are available to protect the polymer before the polymer undergoes vigorous thermal decomposition. To date, there are only a handful of these systems, which show some promise [63], but there is still much to be done with these materials before they are more successful outside their current niche applications [64].

3.7.4 Vapor Phase Flame Retardant

The last new technology, which may come in the future, would be new vapor phase flame retardants. Currently, this is dominated by halogen, but some other elements have been found to show some vapor phase flame retardant activity, namely phosphorus, and a few metals (tin, iron, manganese) [65] in select forms. However, that appears to be the limit of what has been discovered to date as vapor phase flame retardants. So, if halogen is deselected from use and phosphorus is likewise limited, this just about depletes the choices of vapor phase flame retardants available for use [66].

The aforementioned metal-based vapor phase flame retardants in this paragraph unfortunately are only lab curiosities because they are toxic metal carbonyl compounds. To eliminate an entire flame retardant mechanism (vapor phase) would severely limit the ability to flame retard polymeric materials, and so research in this area is sorely needed. Because this area is so crucial, it seems that it is likely that eventually some new vapor phase flame retardants will be discovered in the future, or someone will discover environmentally friendly and economically viable versions of halogenated flame retardants that can be used instead. Admittedly, this prediction of future flame retardant technology is the hardest to predict and define, but still it seems that something in this area is likely to come out in the coming years [67].

3.7.5 Flame Retardant Synergy

In order to achieve high fire performance levels, it is necessary to develop a flame retardant system based on a combination of different flame retardant agents. The concept of synergism is used to optimize flame retardant formulations and enhance the performance of mixtures of two or more additives. Synergism is achieved when the performance level due to a mixture of additives [68].

As discussed above, polymer flame retardancy can be achieved through one or more chemical and/or physical mechanisms taking place in either the gas or the condensed phase. Synergistic phenomena can be obtained either by a combination of flame retardancy mechanisms, such as char formation by a phosphorated flame retardant combined with a gas phase action by a halogenated flame retardant, or by a combination of flame retardant agents reinforcing the same mechanism, e.g. nanoclays and phosphorated flame retardant agents, both acting in the condensed phase.

3.8 Sources of Further Information and Advice

Most of the information in this chapter is general knowledge to those working in the flame retardancy field of polymer materials and is summarized in the list of books and additional references. Sources of further information are listed as follow.

- "A review of current flame retardant systems for epoxy resins" Weil, E. D.; Levchik, S. J. Fire. Sci. 2004, 22, 25–40.
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- “Flame retardants for polystyrenes in commercial use or development” Weil, E. D.; Levchik, S. V. J. Fire Sci. 2007, 25, 241–264.
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- “Fire Properties of Polymer Composite Materials” Eds. Mouritz, A. P.; Gibson, A. G. Springer-Verlag, The Netherlands, 2006. ISBN 978-1-4020-5355-9.
- “Fire Retardancy of Polymeric Materials”, 2nd Edition. Eds. Wilkie, C. A.; Morgan A. B. 2009, Taylor and Francis. ISBN 978–1420083996.
- “Flame Retardants for Plastics and Textiles: Practical Applications” Weil, E. D.; Levchik, S. V. 2009, Hanser Gardner Publications, ISBN 978–1569904541.
- “Fire Retardancy of Polymers: New Strategies and Mechanisms” Hull, T. R.; Kandola B. K. Eds. 2009, Royal Society of Chemistry, ISBN 978–0854041497.

3.9 Conclusion

Stopping the burning of materials is an endeavor as old as recorded history, and as long as we see a need to provide protection against fire, we will have to use flame retardancy in one way or another as a civilization.

Flame retardancy is a much applied field and so understanding all the nuances of the technology is essential to understanding why a particular flame retardant is in use today, as well as what its specific strengths and weaknesses are in its current use. The field of flame retardancy today is dynamic.

Fundamental studies are still needed, but an understanding of the importance of balancing properties and very complex fire risk scenarios and polymer combustion concepts need to be mastered by researchers before they can develop new flame retardant technologies. However, if the reader is just interested in learning the how and why of flame retardant technology, rather than trying to develop a new technology, it is our hope that this review will serve that role nicely.

The flame retardant additive technologies used today may not be utilized in the future. They are suitable and proven for flame retardancy in their respective polymers, but they are not the pinnacles of their respective chemistries; new flame retardant chemistry is likely to be discovered and exploited as more time and money are spent researching this area.

It should be pointed out that, for the most part, flame retardancy is not a topic that most people think about because of successful protection of society provided by the current use of passive flame retardant additives. Fire damages and losses have been reduced by the use of flame retardant additives.

The current trend is to incorporate more rather than less polymeric materials into our modern civilizations, and then new flame retardants will have to be created to address these new tests. Likewise, if improved recycling and lower environmental impact is desired, then new flame retardants will have to be made to meet these requirements. Flame retardant technology is driven by external forces, and these new external forces will greatly change the technology as we know it.

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Chapter 4
Recent Development of Phosphorus Flame Retardants in Thermoplastic Blends and Nanocomposites

Ivana Mihajlović

Abstract With the increasing use of thermoplastics and thermosetting polymers on a large scale for applications in buildings, transportation, electrical engineering and electronics, as well as the high fires safety standards which polymer resins should meet, a large variety of flame retardant products have been developed over the past 40 years. Restrictions on the use of polybrominated diphenyl ethers (PBDE) have resulted in the increased use of alternate flame retardant chemicals, such as phosphorus flame retardants (PFR). PFR contains a wide group of different organic and inorganic compounds, with a great variation in their physico-chemical properties. They are non-flammable, non-explosive and odorless substances listed as High Production Volume Chemicals (HPV). Non-halogen, phosphorus-containing flame retardants such as ammonium polyphosphate and red phosphorus are shown to be very effective in thermoset resins. Phosphate esters significantly lower the heat distortion temperature and impact properties of PC/ABS blends while increasing melt flow in so called antiplasticization process. Resorcinol diphosphate (RDP) was the first material developed for PC/ABS and it is a liquid additive with 9 % P content and good efficacy as a flame retardant. Bisphenol A bisphosphate (BADP) is another liquid with properties similar to RDP. Polymer–clay nanocomposites have attracted a great deal of interest due to their improved mechanical, thermal and biodegradability properties. Nano "sponge" structures produced from cyclodextrins have been tested with flame retardants ammonium polyphosphate (APP) and triethylphopshate. The PFRs can be enclosed in the nano sugar sponge structure, improving mixing with plastic polymers and enabling high flame retardant loadings without deteriorating

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polymer mechanical performance. Fire performance tests using the nano sugar sponge—PFR combination (heat release, heat of combustion, mass loss, smoke) showed that the combination was effective for environmentally friendly structures polypropylene, linear low density polyethylene and polyamide 6.

4.1 Introduction

Flame retardants are widely used all over the world in order to meet flammability standards for various materials (furniture, plastics, electronics equipment, textiles, polyurethane foams, coatings etc.). Since fire causes a lot of injuries and deaths e.g. recorded fires in 2001 caused 2,905 deaths in the six largest EU countries [1], usage of flame retardants is obviously needed. With the increasing use of thermoplastics and thermosetting polymers on a large scale for applications in buildings, transportation, electrical engineering and electronics, a large variety of flame retardant products have been developed over the past 40 years.

Around 90 % of the world's production of flame retardants ends up in electronics and plastics, while the remaining 10 % ends up in coated fabrics and upholstery furniture and bedding products. Flammability of electronics is one particular safety concern that can be mitigated by the appropriate selection of materials used to construct electronic products. Flammability is a concern since unforeseen shorts (unintended electrical connections) can lead to thermal runaways sufficient to ignite a fire. To mitigate this risk, flame-retardants are incorporated into materials such as plastic encapsulants and printed wiring board laminates used to package and construct electronic products. The purpose is to prevent fires, resulting from unanticipated electrical connections, called shorts, which can generate high currents and cause extreme temperature conditions. Flame retardants used in electronic products must comply with the industry flammability standard, Underwriters Laboratories (UL) 94 V-0. In the most common plastic encapsulants, such as epoxy cresol novolac (ECN) and tetrabromobisphenol A (TBBA) epoxy [2, 3], the halide class of brominated flame retardants (BFRs) have been the most widely used due to their low cost. However, BFRs have been considered to be environmentally unfriendly [4]. Therefore, phosphorus-based flame-retardants have been considered as an appropriate replacement to brominated flame retardants, especially to tetrabromobisphenol A. Outside the electronics industry, the use of phosphorus and phosphorus-based compounds as flame-retardants is quite common, with phosphorus-based flame-retardants comprising a 24 % share of the worldwide market [5].

Phosphorus-containing flame retardants cover a wide range of inorganic and organic compounds and include both reactive products which are chemically bound into the polymer material as well as additive products which are integrated into the material by physical mixing only. They have a broad range of applications, and a good fire safety performance. The most important phosphorus-containing flame retardants are phosphate esters, phosphonates and phosphinates (Fig. 4.1).

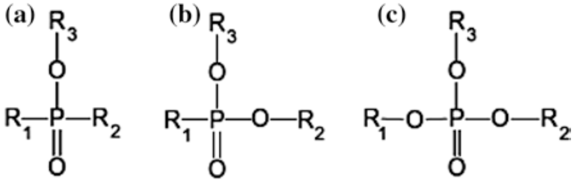

Fig. 4.1 Groups of the most important phosphorus-containing flame retardants: **a** phosphate esters, **b** phosphonates and **c** phosphinates. R_1, R_2, R_3 present alkyl groups

Since the ban on some brominated flame retardants (BFRs), phosphorus flame retardants (PFRs), which were responsible for 20 % of the flame retardant (FR) consumption (11 % chlorinated PFRs and 9 % non halogen PFRs) in 2006 in Europe, are often proposed as alternatives for BFRs. Restrictions on the use of polybrominated diphenyl ethers (PBDE) have resulted in the increased use of alternate flame retardant chemicals, such as organophosphate flame retardants (OFR) [6]. The consumption of FR in Europe in 2006 was estimated to 465,000 metric tons [7]. The most of these compounds are listed as High Production Volume Chemicals (HPV) [8].

Several chlorinated OFR are included in the EU risk assessments: tris(2-chloroethyl) phosphate (TCEP) in the 2nd ESR Priority List, tris(2-chlorisopropyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCP) in the 4th ESR Priority List [9–11]. It was shown that TCEP has carcinogenic and teratogenic effects on organisms [12]. TCEP has demonstrated moderate toxicity after oral application, with oral LD50 for rats in the range of 430–1,230 mg/kg bwt [11]. Studies in rats indicated that TCPP is of moderate toxicity via the oral route of exposure, with LD50 values ranging from 632 up to 4,200 mg/kg [9]. The substance manufacturers have classified TDCP as a category 3 carcinogen for humans [13]. Also, the degradation products of these OFR include the moderately toxic byproduct, 2-ethylhexanoic acid [14]. Clinical signs of maternal toxicity in rats with 2-ethylhexanoic acid, including increased liver weight, as well as increased resorptions, dead fetuses and growth retardation were observed at 500 mg/kg/day [15].

4.2 Phosphorus Flame Retardants

Phosphorus-based flame-retardants can be characterized by their chemical structure and how they are incorporated into the epoxy molding compounds. They are usually divided into two categories: (1) inorganic derivatives: for example, ammonium polyphosphate and red phosphorus; and (2) organic derivatives such as aromatic phosphates: for example, triphenyl phosphate; alkyl substituted triaryl phosphates such as cresyl diphenyl phosphate, isopropyl phenyldiphenyl phosphate, tert-butylphenyldiphenyl phosphate, tricresyl phosphate, trixylyl phosphate, and so on, and oligomeric phosphates such as resorcinol bis(dipheny1 phosphate) (RDP). Special group of phosphorus flame retardants is group of halogen containing PFRs. Halogenated phosphate esters are widely used. They combine the properties of both the halogen and the phosphorus components. The presence of the halogen also increases the lifetime of the flame retardant in the end-product by decreasing its mobility in the polymer. Tris(1-chloroisopropyl) phosphate, used in polyurethane foams, and tris(2- chloroethyl) phosphate, used in several plastics, are the most used examples. All of these groups have been studied as flame retardants with varying degree of success.

Organophosphates are usually mechanically blended, often in liquid form, into resin formulations. Additive organic phosphorus compounds can act as plasticizers and have been reported to have a deleterious effect on the thermo mechanical properties of the epoxy resins. In addition, the organic phosphorus compounds tend to increase the water absorbing property of the plastic encapsulant [16], increasing the probably of pop corning and moisture-related failure mechanisms. Organic phosphorus compounds can be reacted directly into the polymer chain. Investigations have reported success in introducing phosphorus-containing functional groups into the backbones of epoxy. One of the advantages of organic phosphorus is that its reaction products with ambient humidity tend to be non-corrosive phosphorus compounds. This is not always the case with inorganic phosphorus.

Inorganic phosphorus compounds include red phosphorus and ammonium polyphosphate, with red phosphorus being most common in electronic applications. **Red phosphorus** is one of three allotropic forms of elemental phosphorus, with the others being white (or yellow) and black (or violet). Red phosphorus can be formed by heating white phosphorus above 250 °C or by exposing white phosphorus to light. These processes cause the tetrahedral structures of white phosphorus to be chemically re-arranged into a chain of non-periodic five- and six-membered rings, with some additional cross-linking.

Red phosphorus has been reported to be most efficient as a flame retardant in oxygen containing polymers such as polycarbonates, polyethylene terephatalate (PET), polyamide and phenolic resins. Red phosphorus has been used as a flame retardant in polymeric material for almost 30 years [17]. Flame retardancy takes place due to formation of phosphorus-oxygen bonds that reduces the ester linkages into cross linking aromatic structures with lesser volatility. In addition the red phosphorus creates a heat shield on the polymer surface that results in flame retardant properties. Some drawbacks with the use of red phosphorus are the red colour that could lead to discoloration of polymers and the formation of toxic phosphine gas during combustion and long term storage.

Red phosphorus can be a very effective flame retardant for plastics: it is effective at low levels and excellent mechanical properties of the matrix are maintained. For electrical and electronic components, red phosphorus could be the ideal flame retardant because of its good electrical properties—low surface conductivity and high tracking resistance. However, handling and processing safety concerns limit its use. Special retardation and stabilization by microencapsulation is necessary to produce a useful commercial additive. Red phosphorus is very effective in polymers such as polyesters, polyamides and polyurethane, it is used in small quantities (less than 10 %). A typical example is glass-filled PA-6,6 containing 6–8 % red phosphorus, which achieves V-0 classification in the UL 94 test.

Ammonium Polyphosphate, a polymeric flame retardant is used in intumescent coatings and paints. In plastics, if formulated as the only flame-retardant additive in the formulation, it mostly has applications in thermoset resins such as epoxy and unsaturated polyester resins. APP has very good thermal stability and can be used in high-temperature applications. In polyurethane rigid foams, it also finds use when low smoke density and resistance to migration are required. Microencapsulation with melamine produces a useful product for polyurethane foams (e.g. Exolit AP 462). Combined with pentaerythritol as a synergist, or another polyol, it can be used in polypropylene or polyethylene. APP is also suitable for use in hot melt adhesives or coating applications.

Phosphate esters are classified into three types, mainly, triaryl, alkyldiaryl, and trialkyl phosphates. Triaryl phosphates are further classified as natural, if they are produced from naturally derived alcohols (cresols and xylenols), or synthetic, if they are produced from synthetic alcohols (isopropyl phenol and t-butyl phenol). Bisphosphates [such as resorcinol diphosphate (RDP) and bisphenol A diphosphate (BAPP or BADP)] cause significantly less stress cracking in polycarbonate compared to TPP and their usage has expanded significantly in the last 5 years. Phosphate esters are not very stable hydrolytically. RDP is less stable than BAPP. Phosphine oxides are much more stable thermally and hydrolytically than phosphate esters. The P-C bond is very stable and can have unique applications in nylons and polyesters.

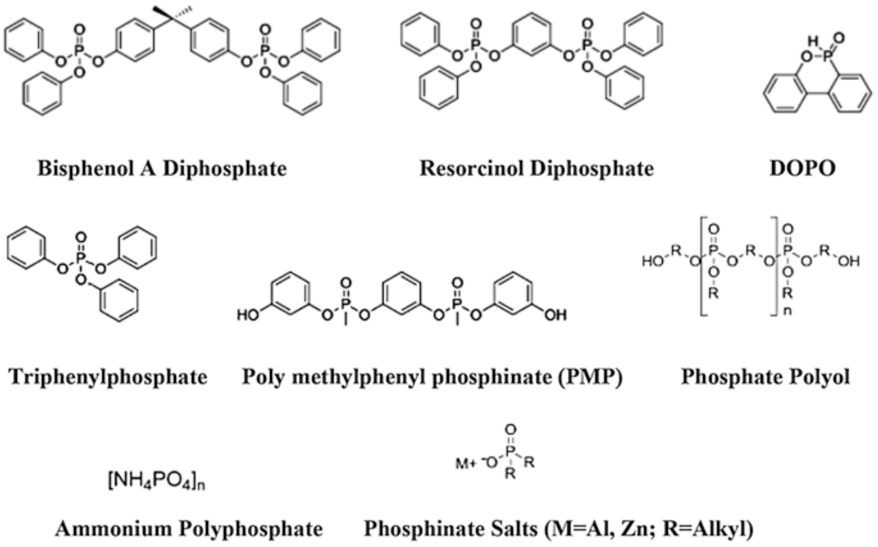

Fig. 4.2 The most widely used compounds of PFR

PFR can be both in vapor phase and condensed phase and can be very effective at lowering heat release rate at low loadings of additive. However, PFR tend to generate more smoke and carbon monoxide during burning, are not effective in all polymers and are also under some regulatory scrutiny. The most widely used compounds of PFR are presented in Fig. 4.2.

4.3 Commercial Products

Phosphorus flame retardants are widely used as adhesives and sealants, for building and construction, as lubricating fluids and greases, in paints and coatings as well as in thermoplastic materials. Key applications of PFR are in EPDM (ethylene propylene diene monomer) rubbers, PVC products, polystyrene, polyurethane foam, epoxy and phenolic resins.

Production process of PFR is based on reaction of phosphorus oxychloride with an organic epoxide in the presence of a catalyst. The product is then washed and dehydrated to remove impurities, filtered and transferred to storage tanks [9–11].

Ban of brominated diphenyl ethers (BDE)—penta-BDE and octa-BDE in the EU and the entry into force of the Restriction of Certain Hazardous Substances caused higher consumption of alternative flame retardants [6]. Global consumption of PFR was estimated to 186,000 tons per year in 2001. In the European Union (EU), their consumption raised from 58,000 tons in 1995 to 91,000 tons in 2006 [7]. The annual consumption of PFR in EU (alkyl phosphates as plasticizers not included) increased for 8 % for only 2 years (from 84,000 tons in 2004 to 91,000 tons in 2006, of which 56 % were chlorinated phosphates) and even greater consumption of these alternative flame retardants could be expected in the last years because of increasing global demand of fire protected materials and products.

The most known manufacturers of PFR are Albemarle Corporation, Great Lakes Chemical Corporation, Supresta (Akzo Nobel) and Cellular Technology international. PFR manufacturers and their commercial products are presented in Table 4.1. Based on triaryl phosphate isopropylated, resorcinal bis-(diphenyl phosphate) or bisphenol a bis-(diphenyl phosphate), these products offer dual functionality as plasticizing agents and flame retardants. They provide increased processing speeds, reduce processing temperatures, and improve compatibility with other additives while also providing superior flame retardant properties. Several halogen containing PFR are commercially available as shown in Table 4.1.

The Great Lakes Chemical Corporation products are Emerald Innovation™ NH-1, Reofos 35/50/LF-50/65/95/RDP/BAPP, Kronitex CDP/TCP/TXP and Firemaster® 550/552.

Emerald Innovation™ NH-1 is effective, halogen-free flame retardant for polyurethane foam that offers superior scorches resistance, reduced fogging/emissions and better long-term renting.

Reofos 35 (Isopropylate Triphenyl Phosphate; Isopropyl Phenyl Diphenyl Phosphate; Tri (isopropylphenyl) Phosphate) with CAS NO. 68937-41-7 and

Table 4.1 Commercial products of PFR

Albemarle corporation	Great lakes chemical corporation	Supresta (Akzo Nobel)	Cellular technology international
SAYTEX® RX-8500	Firemaster® 550	Fyrol® FR-2	IPPP-35
CAS 115-86-6		CAS 136774-87-8	
SAYTEX® RZ-243	Firemaster® 552	AB053	IPPP-50
ANTIBLAZE® 180	Emerald Innovation™ NH-1	AC003	IPPP-65
CAS 13674-87-8			
ANTIBLAZE® 182	Reofos® 35	AC073	IPPP-95
	CAS 68937-41-7		
ANTIBLAZE® 195	Reofos® 50	Ferquel 150	HF-4
CAS 13674-87-8			
ANTIBLAZE® 205	Reofos® LF-50	Ferquel 220	HF-4L
ANTIBLAZE® V-500	Reofos® 65	Ferquel 300	
ANTIBLAZE® TL10ST	Reofos® 95		
	Reofos® RDP		
	Reofos® BAPP		
	Kronitex® CDP		
	Kronitex® TCP		
	Kronitex® TXP		

molecular formula C27H33O4P is a low viscosity synthetic isopropylated triaryl phosphate ester that finds utility in a wide variety of applications as a flame-retardant plasticizer, suitable in plastisols for fabric coating where a drier finish is desired, also designed for use in phenolic laminates.

Reofos® 50 is a synthetic isopropylated triaryl phosphate ester, which can be used in a wide variety of resins, particularly PVC. Reofos® 50 is recommended as a flame retardant for PVC, flexible polyurethanes, cellulosic resins, and synthetic rubber, as a flame retardant processing aid for engineering resins, such as modified PPO, polycarbonate and polycarbonate blends. Reofos® 65 is synthetic isopropylated triaryl phosphate ester that acts as a flame-retardant plasticizer or processing aid, especially suited for PVC and phenolic resins. Reofos® 95 is flame retardant plasticizer used primarily in PVC, phenolic resins, flexible polyurethane, cellulosics, synthetic rubber and other engineering resins. Reofos® BAPP are liquid phosphate ester flame retardants for thermoplastics, especially well-suited for styrene blends [18].

SAYTEX® RX-8500 consists of proprietary reactive brominated flame retardant, proprietary aryl phosphate and triphenyl phosphate, while SAYTEX® RZ-243 contains proprietary tetrabromophthalate, proprietary aryl phosphate and triphenyl phosphate. ANTIBLAZE® 180 and ANTIBLAZE® 195 from Albemarle corporation as well as Fyrol® FR-2 and AB053 from Supresta consist of tris (1,3-dichloro-2-propyl) phosphate. ANTIBLAZE® 182, ANTIBLAZE® 205 and ANTIBLAZE® V-500 are made of proprietary chloroalkyl phosphate, aryl phosphate and triphenyl phosphate.

Ferquel 150, Ferquel 220 and Ferquel 300 are all made of butylated triphenyl phosphate esters. Proprietary organic phosphate ester and triphenyl phosphate form AC003, and similar proprietary aryl phosphates and triphenyl phosphate are used for AC073.

Cellular Technology International, and European subsidiary Cellular Technology Europe Ltd have added a broad range of flame retardant plasticizers with wide application for polyurethane and vinyl. The CELLTECH IPPP product range is a family of isopropylated phenyl phosphates, identical to the widely used REOFOS line. The commercial products known as IPPP-35, IPPP-50, IPPP-65 and IPPP-95 are equivalent respectively to REOFOS 35, 50, 65 and 95. Isopropylated phenyl phosphates are used as flame retardant plasticizers in flexible polyurethane foam and in vinyl applications such as mine belting, and vinyl sheeting. IPPP35 is halogen-free flame retardant phosphate ester plasticizer, widely used for fabric coating, circuit boards, flooring, textiles, PVC, phenolic resin, and other fields. CELLTECH HF-4 and HF-4L are tert-butylated phenyl phosphates also recommended for polymer applications such as polyurethane and vinyl, and also are widely used as functional hydraulic fluids. CELLTECH HF-4 is equivalent to REOFOS 507, PHOSFLEX 71B and SANTICIZER 154; CELLTECH HF-4L is a low-TPP content version of HF-4, equivalent to PHOSFLEX 71B Plus [19].

4.4 Degradation of Phosphorus Flame Retardants

Thermal degradation is an important process during the combustion of polymers. The degradation can be divided into pyrolysis and thermal oxidative degradation (TOD). TOD means that thermal degradation occurs in the presence of oxygen, whereas pyrolysis takes place when thermal degradation occurs at high temperatures in the absence of oxygen. The techniques commonly used to study the thermal degradation include thermogravemetric (TG), differential scanning calorimetry (DSC), pyrolysis gas chromatography (Py-GC) or pyrolysis gas chromatography mass spectrometry (Py-GC/MS) [20].

Most of the PFRs have a mechanism of action in the solid phase of burning materials (char formation), but some may also be active in the gas phase. Some PFRs are reactive FRs, which means they are chemically bound to a polymer, whereas others are additive and mixed into the polymer. Phosphorus-based flame-retardants impede the combustion process through multiple reaction steps. PFR can remain in the solid phase and promote charring or volatize into the gas phase, where they form active radicals ($PO_2^\bullet$, $PO^\bullet$ and $HPO^\bullet$), and act as scavengers of $H^\bullet$ and $OH^\bullet$. In the condensed phase, the phosphorus-based flame retardants are particularly effective with polymers containing oxygen or nitrogen (polyesters, polyamides, cellulose, etc.). Volatile PFRs are among the most effective combustion inhibitors since phosphorus-based radicals are, at the same molar, five times more effective than bromine and 10 times more effective than chlorine radicals.

During exposure to the high temperature of ignition, the phosphorus-containing functional groups are converted to phosphoric acid by thermal decomposition [21]. Phosphoric acid causes the material to char, forming a glassy layer and inhibiting the "pyrolysis" process (break down and release of flammable gases) which is necessary to feed flames. Except of phosphoric acid, during thermal degradation liberate water was also released. The water released dilutes the oxidizing gas phase. In addition, phosphoric acid and pyrophosphoric acid can catalyze the dehydration reaction of the terminal alcohols leading to the formation of carbocations and carbon–carbon double bonds. At high temperature, this can subsequently result in the generation of cross linked or carbonized structures. Ortho- and pyrophosphoric acids are turned into metaphosphoric acid and their corresponding polymers. The phosphate anions (pyro- and polyphosphates) then take part, with the carbonized residues, in char formation. By this mode of action the amount of fuel produced is significantly diminished, because char rather than combustible gas is formed. The intumescent char plays particular roles in the flame retardant process. It acts as a 2-way barrier, both hindering the passage of the combustible gases and molten polymer towards the flame, and shielding the polymer from the heat of the flame [7]. This carbonized layer (char) isolates and protects the polymer from the flames and limits the volatilization of fuel, prevents the formation of new free-radicals; limits oxygen diffusion, which reduces combustion; insulates the polymer underneath from the heat.

Except of thermal degradation, PFR could be degraded by microorganisms. In soil and sediment, chlorinated PFR (TCEP, TCPP and TDCP) were considered to be persistent as they have a tendency to adsorb strongly and thus limited availability to microorganisms [22]. Non halogenated PFR are degraded by microorganisms in activated sludge [23, 24]. Standard biodegradation tests indicated that TnBP, TBEP and TPP are readily biodegradable, but TCPP and TDCP have been shown to be not readily biodegradable [6, 9–11, 24]. TBEP when tested in the OECD 301B essay, achieved 87 % degradation within 28 days [25]. The biodegradation of TnBP is moderate or slow depending on the ratio of TnBP to active biomass. It involves stepwise enzymatic hydrolysis to orthophosphate and n-butanol, which undergoes further degradation [23]. TPP has a high potential for bioaccumulation, because of its hydrophobicity. Under anaerobic soil conditions, TPP had a half-life of 32 days, while commercial soil produced nearly quantitative recovery of TPP after 101 days [26]. TCEP has been considered as non-biodegradable in EU Risk Assessment document [11] however in the last years bacterial strains, Sphingobium sp. TCM1 and Sphingomonas sp. TDK1, were isolated from soil and it was proved that TCEP and TDCP could degrade by hydrolyzing their phosphotriester bonds [27]. The strains are the first microorganisms reported to degrade the persistent PFRs. They degrade the compounds by hydrolyzing their phosphotriester bonds to produce metabolites 1,3-DCP from TDCP and 2-CE from TCEP, which are themselves toxic and non-self-biodegradable. TCM1 was then combined with the 1,3-DCP-degrading bacterium Arthrobacter sp. strain PY1 (for TDCP degradation), and with the 2-CE-degrading bacterium X. autotrophicus strain GJ10 (for TCEP degradation) and degradation products of TDCP and TCEP were successfully detoxified [28].

Bisphenol A could be metabolized by a Gram-negative aerobic bacterium (strain MV1) via a novel pathway involving oxidative skeletal rearrangement. The metabolism involves two primary pathways: a minor pathway, in which Bisphenol A is first oxidized to a triol, and a major pathway, in which Bisphenol A is metabolized to form the intermediates 4-hydroxybenzoate and 4-hydroxyacetophenone that are converted to carbon dioxide and biomass. *Sphingobium xenophagium* Bayram and *Sphingomonas* p. strain TTNP3 can metabolize bisphenol A by an *ipso*-substitution mechanism that involves ring hydroxylation at the site of the substituent. This proposed hydroxylation product can be cleaved to form hydroquinone and a proposed 2-(4-hydroxyphenyl)-isopropyl cation. The cation can be transformed to 4-(2-hydroxypropan-2-yl) phenol, which can eliminate water to form 4-isopropenylphenol. 4-Isopropenylphenol can be reduced to 4-isopropylphenol. There are other possible routes of bisphenol A degradation, including formation of a 2-(4-hydroxyphenyl)-isopropyl anion instead of the cation, to the above products, and other side reactions occur in one organism or the other [29].

4.5 Applications of Phosphorus Flame Retardants

In many applications, rigid and flexible polyurethane foams are required to exhibit a degree of flammability resistance in order to pass specific flammability tests in any given country. Phosphorus based flame retardants, both chlorinated (chlorophosphates) and non-halogenated are extensively used in these applications and are considered an ideal choice, giving a good balance of process ability, flame retardancy and physical properties. In some instances phosphorous bromine blends are used particularly where low scorch is required. Depending on the final application, its key requirements and the flammability standards they must meet, PUR foam producers have the flexibility to choose among reactive additive, halogenated and non-halogenated phosphorus based flame retardants. These options provide a versatile selection for addressing the market needs of: performance, compatibility, efficiency, physical properties, process ability and cost.

Electrical systems are estimated to be the cause of around one fifth of all fires. Electrical faults like short-circuiting and arcing release sufficient energy to ignite commonly used polymers in electronic equipment, household appliances or electrical installations. Therefore, safety requirements demand the use of flame resistant materials in proximity to live parts, connectors etc. In addition to using metals or ceramics, flame retarded polymers are often chosen, because they have excellent technical properties and are economically attractive.

Fire safety is an essential element in building and constructions. Several national and international fire standards regulate the reaction to fire (ignition time, flame spread, smoke density, toxicity of gases) of materials used in this industry. In order to meet these fire safety requirements the use of flame retardants is often necessary especially in polymeric types of materials, e.g. in insulation, pipes and cables. The selection of the appropriate products depends mainly on the material and the required fire standard. Intumescent coatings based on PIN flame retardants ensure the stability of steel structures in case of a fire for a defined period of time (fire resistance), because steel can lose its strength at temperatures above 500 °C.

Transport vehicles like aeroplanes, ships, trains, busses and cars must provide a sufficient level of fire safety. The possibility for people to quickly evacuate the vehicle in case of fire is severely limited for aeroplanes, ships or trains, but even for cars it can be difficult in the case of an accident. Flame retardants prevent the ignition of otherwise highly flammable textile covers on seats including their upholstery fillings, curtains as well as wall panels and other structural parts. The fire safety standards for "high risk" transport systems like aeroplanes and trains also include requirements on the toxicity of smoke and combustion products.

The flammability of textiles ranges from easily ignitable cotton or polyester materials to virtually non-flammable high performance textiles based on aramides. The ignitability depends not only on the material itself, but also on the density/thickness of the fabric and adjacent materials, e.g. when used as an upholstered furniture cover. Flame retardants can be used to limit the flammability of textiles by reacting co-monomers into synthetic polymer materials, treating the surface of the fibres or coating the finished textile with a flame retardant formulation. The desired or required durability against wear and washing is a key criterion for choosing the appropriate textile and flame retardant combination.

Phosphorus-containing flame retardants (PFRs) have been used as effective flame retardants; the range of PFRs is extremely wide and diverse, since the element exists in several oxidation states. PFRs are widely used in standard and engineering plastics, polyurethane foams, thermosets, coatings, and textiles [30, 31]. Phosphate esters are mainly used as flame retardant plasticizers in polyvinylchloride (PVC, alkyl/aryl phosphates) and engineering plastics, particularly in polyphenylene oxide/high impact polystyrene (PPO/HIPS), polycarbonate/acrylonitrile butadiene styrene (PC/ABS) blends and polycarbonate (PC, e.g. triphenylphosphate, resocinol- and bisphenol A- bis-(diphenyl) phosphate). The latter are widely used in IT housings requiring high fire safety levels. Other applications include phenolic resins and coatings. Phosphates, phosphonates and phosphinates are used as reactive phosphorus containing flame retardants in flexible polyurethane foams for automotive and building applications. Additive organic phosphinates are a new class of flame retardants for use in engineering plastics, particularly in polyamides. Specific reactive phosphorus flame retardants are used in polyester fibres and for wash resistant flame retardant textile finishes. Other reactive organophosphorus compounds can be used in epoxy resins in printed circuit boards.

Red phosphorus and ammonium polyphosphate (APP) are used in various plastics. Red phosphorus was first investigated in polyurethane foams and found to be very effective as a flame retardant. It is now used particularly for polyamides and phenolic applications. The flame-retarding effect is due, in all probability, to the oxidation of elemental phosphorus during the combustion process to phosphoric acid or phosphorus pentoxide. Flame retardant grades based on red phosphorus are mainly used in glass fibre reinforced polyamide 6 and 66. Further applications are in polyethylene and ethylene vinyl acetate (EVA), polyurethane foam, and thermosettings resins (unsaturated polyesters and epoxies). Ammonium polyphosphate grades are primarily used in intumescent coatings. They are also found in rigid and flexible polyurethane foams and polyolefins (injection moulded), in formulations for unsaturated polyesters, phenolics, epoxies and coatings for textiles [32].

TnBP and TPP, are used as additives in hydraulic fluids, lubricants, transmission and motor oils [23, 33]. TBEP is used in floor polishes, as antifoaming agent and as a plasticizer in rubber and plastics [24]. TCEP is mainly used as a flame retardant in the production of polyurethane foam (around 80 %) e.g. as roof insulation for the building industry. The other applications are as plasticizer in furniture, the textile and the building industry as well as in acrylic resins, adhesives and coatings (≈20 %) [11]. Most TCPP is used in rigid PUR foam (over 80 %) mainly for construction applications. The remaining PUR applications are accounted for flexible foam (over 17 %), used in upholstery and bedding for the UK and Irish markets. TCPP tends not to be used in flexible PUR for automotive applications, owing to its volatility and fogging potential.

TDCP could be used in the same application fields as TCPP, but comparing the price (around twice the price of TCPP), TDCP is only used when a more efficient flame retardant is required to meet specific standards. TDCP is mostly used in PUR foams in the automotive industry (about 80 %), with some use in furniture (about 20 %) [10].

Dimethyl methyl phosphonate (DMMP) is used in rigid foam applications that allow the addition of the flame retardant to the foam components immediately prior to or during the manufacturing process. Its high phosphorus content (25 %) makes it ideal for rigid polyurethane, or polyester hybrids using hydrocarbon blowing agents. In unsaturated polyester resins, it can be used as a replacement for inorganic flame retardants.

Cyclic phosphonates (such as Antiblaze N for textiles or Antiblaze 1045 for plastic applications) are high-phosphorus-content, glass-type liquid additives (21 % P). These cyclic phosphonates can be used in epoxies, unfilled thermoplastic polyesters, polycarbonates, and niche polyamides. Reinforced epoxy composites with good retention of mechanical properties can be achieved with 8–15 % loadings depending on resins and curing agents. Flame-retardant PET can be produced with 3–5 % addition levels.

Ethylene diamine phosphate (EDAP) is an important additive for achieving halogen free flame retardancy in polyolefins. It is a neutral compound in aqueous systems and is compatible with coadditives used in curable systems such as urethanes and epoxies. Its major disadvantage is its thermal stability—it decomposes at temperatures above 250 °C and in practical applications temperatures have to be kept close to 200 °C.

Monophosphates have been used mainly in PVC as flame-retardant plasticizers and up to the 1970s in PPO/HIPS blends. Bisphosphates (such as resorcinol diphosphate and bisphenol A diphosphate) are mainly used in PC/ABS blends. Bisphenol A is widely used as a monomer for the production of polymers, such as epoxy resins and polycarbonate plastics. These plastics are used in many foods and drink packaging applications. When the resins are inert materials, they are commonly used as lacquers to coat metal products such as food cans, bottle tops and water supply pipes.

Phosphine oxide diols can be polymerized into polyesters [PBT, PET], polycarbonates, epoxy resins, and polyurethanes. An alkyl bishydroxymethyl phosphine oxide may be in use today for epoxy circuit printed boards. Phosphine oxides are expensive and this significantly limits their application.

Phosphonates are used in various thermoplastic and thermoset applications. Products such as Antiblaze V490 are used in laminates and block foams. They are suitable for formulations employing CFC, HCFCs, water, or hydrocarbon blowing agents. Added into two-component foam systems, the phosphonate functions as a viscosity depressant, improving the processing characteristics of formulations utilizing water-blown or polyester polyols.

Melamine phosphate is used in conjunction with other organophosphorus compounds in olefins and thermoplastic urethanes. Melamine polyphosphate has recently become available (Melapur MP200 from DSM) and can be used in reinforced polyamides and polyesters, epoxies, and thermoplastic urethanes.

4.6 Properties of Phosphorus Flame Retardants

Since PFR contains a wide group of different organic and inorganic compounds, there is a great variation in their physico-chemical properties. PFR are non-flammable, non-explosive and odorless substances. However, some of them, di-ammonium phosphate (DAP), dimethyl methyl phosphonate (DMMP) and TCEP are highly soluble in water, while trixylenyl phosphate (TXP), isodecyldiphenyl phosphate (IDPP) and TPP are immiscible with water. The solubility of PFR decreases by increasing their molecular mass. Most of the PFRs have a positive log Kow value, which means they are more lipophilic than hydrophilic. The log Kow values vary considerably between the different PFR groups. The selected PFR obtain a wide range of Henry's Law constants (from 0.323 to 10^{-18} Pa m^3/mol) indicating high variability in distribution of PFRs over air and water. There is also a great variability in vapor pressures and bioconcentration factors for different compounds of PFRs. BCF ranges from 1.37 for TCEP to 10^6 for trioctyl phosphate and tris(2-ethylhexyl)phosphate (TEHP) [34].

The properties of polymers, e.g. ammonium polyphosphate depend on the number of monomers in each molecule and to a degree on how often it branches. Shorter chains ($n < 100$) are more water sensitive and less thermally stable than longer chains ($n > 1{,}000$), but short polymer chains (e.g. pyro-, tripoly-, and tetrapoly-) are more soluble and show increasing solubility with increasing chain length.

RDP is a colorless to light yellow liquid product with phosphorus content of 10.8 %, which is higher than in triphenyl phosphate and an important advantage since flame-retardancy properties are directly related to the phosphorus level. RDP is very poorly soluble in water and has a very high log Kow of 7.41 [35]. RDP is thermally stable [36], it decomposes above 300 °C.

BADP is an aryl phosphate, active in the condensed phase as well as in the gas phase [37]. BADP has a log Kow of 4.5 [35].

Diethylphosphinic acid is often formed and released during the gas phase, by decomposition of FR materials. Diethylphosphinic acid has a boiling point of 320 °C [38].

TBEP is a light-coloured, high-boiling, non-flammable viscous liquid with a butyl-like odour under normal conditions. It is more soluble in non-polar than in polar solvents with the water solubility of 27 mg/L at 25 °C. From molecular connectivity method, the highest value of soil-sediment water sorption coefficient (log Koc = 5.67) was estimated for TBEP compared to other studied OFR [39].

TnBP is a non-flammable, nonexplosive, colourless and odourless liquid. It is thermally unstable and begins to decompose at temperatures below its boiling point. TnBP has the high vapour pressure (0.150 Pa) and Henry's Law Constant value (0.323 Pa m^3/mol) however it has low water solubility (27 mg/L at 25 °C). Log Kow and log Koc for TnBP are estimated to be 3.82 and 3.28, respectively [39, 40].

TPP is colourless solid with very low water solubility (3 mg/L at 25 °C) and high log Kow value (4.59). Henry's Law Constant from bond method estimation is calculated to 4.03×10^{-3} Pa m^3/mol.

TCP is a non-flammable, clear, faintly yellow, viscous odorless liquid, which is a mixture of mainly three isomers: tri-ortho-cresylphosphate (o-TCP) (cas no. 78-30-8), tri-meta-cresylphosphate (m-TCP) (cas no. 563-04-2), and tri-para-cresylphosphate (p-TCP) (cas no. 78-32-0). TCP has a low water solubility of 0.36 mg/L, and a log Kow of 5.11. In an alkaline medium it can easily be hydrolyzed to dicresylphosphate and cresol, but it is stable in neutral and acidic media [41].

TCEP is liquid at the temperature of 20 °C, with melting point at −70 °C and decomposition at 320 °C and 1,013 Pa. The water solubility at 20 °C varies from 5 to 8 g/L. The water solubility at 25 °C of 7,409 mg/L was estimated from logarithms of octanol-water partitioning coefficient (log K_{ow}) of 1.44. Soil-sediment water sorption coefficient (log K_{oc}) of 2.48 was estimated from molecular connectivity, while value of Henry's law constant (H) of 2.58×10^{-3} (Pa m^3/mol) at 25 °C was obtained from bond method estimation [39, 40].

TCPP is colorless transparent oily liquid with molecular mass of 327.57 g/mol. Three isomers of the main component are possible: bis(1-chloro-2-propyl)-2-chloropropyl phosphate, bis(2-chloropropyl)-1-chloro-2-propyl phosphate and tris(2-chloropropyl) phosphate. Water solubility of TCPP at 25 °C was estimated to be 1,200 mg/L [39, 40]. The preferred value of vapour pressure was 1.4×10^{-3} Pa at 25 °C [42] and Log K_{ow} of 2.68 ± 0.36 was obtained by the HPLC estimation method in a modern GLP study [43]. Log K_{oc} of 2.48 was estimated from molecular connectivity, while value of Henry's Law Constant (6.04×10^{-3} Pa m^3/mol) was obtained from bond method estimation [39, 40].

TDCP is a viscous yellow liquid with molecular mass of 430.91 g/mol, relative density of 1.513 and low water solubility of 29 mg/L at 25 °C [10, 25].

The partition coefficient between octanol and water is 3.69 according to the HPLC estimation method [43], while log K_{oc} was estimated to be 3.96 according to molecular connectivity method.

Tetrekis(2-chlorethyl)dichloroisopentyldiphosphate (V6) is an additive FR, which is in Europe only produced by one producer. V6 was only available with a purity of >90 % and containing TCEP (4.5–7.5 % (w/w)) [9]. Nowadays V6 is available without the impurity of TCEP. V6, TCPP and TDCP have a chemical similarity and a similar use pattern. V6 is only used together with TCPP and TDCP in applications where a more effective FR is required to meet specific criteria. V6 has a boiling point of 620 °C, a solubility in water of 2.1 mg/L, and a log Kow value of 1.9 [44].

Melamine polyphosphate is a salt of melamine and polyphosphoric acid. It decomposes at 350 °C and the phosphoric acid evolved coats and shields the combustible polymer from the heat source as a glassy surface. Melamine in the gas phase dilutes the oxygen and the combustion gases. The amount of gases evolved during combustion of polymers flame retarded with melamine derivatives is significantly lower than that produced when other types of flame retardants are used. Melamine polyphosphate is a phosphorus and nitrogen containing FR, which is chemically built into a polymer molecule. At room temperature melamine polyphosphate is a white, fine crystalline powder with no odor, and a boiling- and melting point higher than 400 °C [45]. Melamine polyphosphate has water solubility lower than 0.1 g/L and a log Kow of 2.3 [46].

4.7 Effects of Phosphorus Flame Retardants in Environment

Many of the PFRs are additives, and not chemically bonded to the final products, which may result in an easy release to the environment from furniture, electronic equipment, carpets, and also into the atmosphere from different sources such as buildings and vehicles [16]. Total continental emissions for TDCP and TCPP were estimated at 15.33 and 89.56 kg/d, respectively. Loss of TCEP to air from outdoor and indoor services results in a total release of 1.30 kg/d [9, 10, 47].

Individual data on the occurrence of PFR in water and air has increased continuously over the last decade. PFR have been already detected in river water, ground water and rain [30, 48, 49], in snow [50], in outdoor air and dust [51], sediments [52] and soil [53]. Limited information is available on the occurrence of PFRs in biota. PFR have also been found in influents and effluents of municipal wastewater treatment plants [54], where they are transported via the sewage system from households, industrial sites, and storm water drainage.

PFR have been the mostly studied in indoor environments such as library, private home, office, prison, day care center and computer hall. Their concentrations in indoor air ranged from less than 0.2–760 ng/m^3. Carlsson et al. [55] found that their concentrations in indoor air depended on the kind and amount of furniture, building material and electronic equipment that are located in the room, the temperature and the degree of ventilation. TCEP concentrations in indoor air were in range from <0.3 to 2,037 ng/m^3 in lecture hall in Sweden [56, 57]. High TCEP concentrations were measured in office (730 ng/m^3), laboratory (367 ng/m^3) and day care center (144 ng/m^3) in Sweden [55, 58]. TDCP, TPP, TnBP and TBEP were measured in low concentration ranges in indoor air in Sweden, 2–7, <0.3–35.3, <0.3–138 and <0.2–130 ng/m^3, respectively. TCPP was detected in very high concentrations in computer hall (1,080 ng/m^3), laboratory (2,836 ng/m^3) and lecture hall (1,118 ng/m^3) in studies conducted in Sweden. The TCEP concentrations are substantially lower than those of TCPP, which probably can be explained by the continuing increase of the use of TCPP and the replacement of TCEP by TCPP as an flame retardant for toxicity reasons [59]. TDCPP was detected in indoor dust in higher concentrations than TCEP and TCPP. The concentration of TCP detected in the lecture room in Sweden was 0.4 ng/m^3, but TCP was not detected in the kindergarten in Sweden and the most of the indoor locations in and around Zurich, Switzerland [60, 61].

In outdoor air and deposition samples, PFR (TnBP, TCEP, TCPP, TDCP and TPP) were detected in Pallas, northern Finland. In the German part of the North Sea, TCPP was detected in concentrations up to 1,200 pg/m^3 [62]. TCPP, TnBP and TBEP were also detected in outdoor air in Tokyo at sampling sites located at verandas or below the eaves of houses and offices with maximum concentrations of 3.1, 1.7 and 1.1 ng/m^3, respectively, whereas TCEP was below the LOD of 0.67 ng/m^3 [63]. V6 concentrations detected in air from Norway were <0.2–5.2 ng/m^3 [64]. Results from laboratory experiments of Regnery and Puttmann [65] showed rapid degradation of TBEP, TBP and TiBP by sunlight. The chlorinated PFRs, TCEP and TCPP, seemed to be resistant to degradation by sunlight. However, concentrations of all studied PFR in outdoor air were much lower than their concentrations in indoor air. European Commission [9–11] estimated half-lives in air for chlorinated PFR shorter than 24 h. Therefore, it could be assumed that most of PFR emitted to the atmosphere, may then be washed out by rainfall [9, 24, 47]. PFR have already been detected in rainwater and snow samples in Italy and Germany in concentrations between 2 and 743 ng/L [49, 50, 66]. Influence of traffic as a source of PFR in snow samples was studied by Marklund et al. [67]. Clear decrease in concentrations, especially for TCPP with increased distance from the road intersection was observed. TnBP and TPP dominated at the airport. The main source of TnBP at the airport was traced to aircraft hydraulic fluid, while TPP was identified in lubricants and in waste oil from vehicles, and thus, leakage of transmission and motor oils could be the source of TPP found at the sampled sites. Regnery and Püttmann [50] assumed that precipitation had an important role as an entry pathway for OFR into the aquatic and terrestrial environment.

In water samples, TBEP was found in the highest concentrations river samples in Germany (952 ng/L) and in Danube, Liesig and Schwechat rivers in Austria (500 ng/L) [49, 68]. In the two volcanic lakes located in Central Italy, TnBP was measured in the highest concentration of 784 ng/L [66]. TCP and V6 were not detected in surface water in the literature studied. Significant source of river pollution could be the discharge of treated wastewater into rivers. It was confirmed in the studies where PFR were measured in very high concentrations. TBEP, TCPP and TnBP were found in effluents from seven Swedish sewage treatment plants in concentrations up to 35000, 30000 and 52000 ng/L, respectively [69]. Meyer and Bester [54] studied PFR in two wastewater treatment plants in Germany, where TBEP, TCPP and TnBP were also detected, with maximum levels of 4000, 2600 and 1100 ng/L, respectively. A partial biological removal of non chlorinated PFR, TnBP and TBEP in wastewater treatment plants was observed [49, 54, 69].

In sediments, high concentration levels up to 7,395 μg/kg for chlorinated PFR (TCEP, TCPP, TDCP) were found by Kawagoshi et al. [70]. High concentrations of TCPP up to 1,300 μg/kg dwt (dry weight) were found in sediments of Danube, Liesig and Schwechat rivers in Austria [68].

In soil samples, TPP was detected in high concentrations from 2 to 6 μg/g dwt at U.S. Air Force Base contaminated with hydraulic fluids [71]. The mobility of TPP in soil is not expected because of low vapour pressure and water solubility and high soil sorption coefficient [26].

Concentrations of TCEP, TCPP and TBEP in soil samples from different areas in Germany varied between LOQ and 18.2, 0.59 and 8.33 ng/g dwt, LOD and 13 n/g dwt, respectively [72]. TCEP is particularly mobile in soil and has the greatest potential to leach into groundwater. Migration during bank filtration/underground passage and presence of TnBP, TCEP, TCPP and TBEP in the groundwater have been reported by Fries and Püttmann [49].

Only a few studies on PFRs in biota are known. Green et al. [64] reported TDCP levels in cod liver from Norway of <5 and <10–30 μg/kg for mussel. Evenset et al. [73] found TDCP and TCEP levels of 5 and 6.7 μg/kg in fish muscle tissue and 6.7 and 26 μg/kg in fish liver. Leonards et al. [74] detected TDCP in bird egg (<0.72–1.9 μg/kg) and in bird blood (<0.11–0.16 μg/kg). No V6 was detected in cod liver and mussel from Norway in 2008 (<20 μg/kg) [64]. In none of the biota samples from Norway analyzed in a study of Leonards et al. [74] V6 was detected either, with LODs varying from <0.01 μg/kg for blood to <0.4 μg/kg for cod liver. PFR concentrations in environment are presented in Table 4.2.

TnBP may enter into the environment by leakage from sites of production or use, as well as by leaching from plastics disposed in landfill sites or aquatic environments. Emission of TBEP is mainly to soil, sediments and surface waters from leachates, plastics on landfills, spillages and effluents. In the environment, TBEP is expected to partition to sediments [24]. Entry of TPP into the environment occurs mainly through leakages from hydraulic equipment. There are no data available on Resorcinol-bis(diphenylphosphate), Bisphenol-A diphenyl phosphate, Diphenylcresylphosphate, Melamine polyphosphate and Diethylphosphinic acid levels in the environment. TCPP is the most dominant PFR present in air, water and sediments, which is explained by its high production volume and its relatively persistent character. TDCP was being the dominant only in dust samples. Only chlorinated PFRs are carcinogenic. In the risk assessment for TCEP [11] it has been concluded that this compound meets the persistent/very persistent (P/vP)- and the toxic (T)-criteria. Other negative human health effects were found

Table 4.2 PFR concentrations in the environment

Matrix	PFR	Location	Concentration levels	References
Indoor air	TCEP	House, Japan	1.3 (ND–136) ng/m^3	[63]
		Office Building, Japan	3.3 (ND–42.1) ng/m^3	[63]
		Computer Hall, Sweden	3 ng/m^3	[57]
		Laboratory, Sweden	367 ng/m^3	[56]
		Lecture Hall, Sweden	2,037 ng/m^3	[56]
		Day Care Center, Sweden	144 ng/m^3	[55]
		New Car, Sweden	109.5 ng/m^3	[91]
		Private home, Sweden	11.4 ng/m^3	[91]
	TCPP	Office Building, Japan	6.0 (ND–57.6) ng/m^3	[63]
		Lecture Hall, Sweden	762 ng/m^3	[57]
		Computer Hall, Sweden	1,080 ng/m^3	[57]
	TPP	Computer Hall, Sweden	1 ng/m^3	[57]
		Dismantling Facility, Sweden	17 ng/m^3	[57]
		Office, Sweden	20.1 ng/m^3	[92]
		Laboratory, Sweden	8 ng/m^3	[56]
		Lecture Hall, Sweden	7 ng/m^3	[56]
	TBEP	House, Japan	1.8 (ND–13.7) ng/m^3	[63]
		Dismantling Facility, Sweden	130 ng/m^3	[57]
		Day Care Center, Sweden	5.9 ng/m^3	[55]
		New car, Sweden	36.4 ng/m^3	[91]
		Private home, Sweden	42.5 ng/m^3	[91]
		Prison, Sweden	55 ng/m^3	[58]
Outdoor air	TCEP	Alnabru, Norway (heavy traffic)	2.4 ng/m^3	[64]
		Svalbard, Archipelago in the Arctic	0.27 ng/m^3	[64]
	TDCP	Alnabru, Norway (heavy traffic)	0.056 ng/m^3	[64]
		Svalbard, Archipelago in the Arctic	0.19 ng/m^3	[64]
	TnBP	Alnabru, Norway (heavy traffic)	1.36 ng/m^3	[64]
	TPP	Alnabru, Norway (heavy traffic)	0.88 ng/m^3	[64]
		Svalbard, Archipelago in the Arctic	<0.05 ng/m^3	[64]
Water	TCEP	Bahnbruecke, Germany, rain water	121 ng/L	[49]
		Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/Main-Germany, rainwater	11–196 ng/L	[50]
		Rome, Martignano Lake, Italy, rainwater	19–161 ng/L	[66]

(continued)

Table 4.2 (continued)

Matrix	PFR	Location	Concentration levels	References
		Urban storm water holding tank (SWHT)	77–104 ng/L	[65]
		Rhine, Elbe, Main, Oder, Nidda and Schwarzbach Rivers, Germany	17–220 ng/L	[48]
		Oder River, Germany	30–1,236 ng/L	[49]
		Danube, Liesig and Schwechat Rivers, Austria	13–130 ng/L	[68]
		Ruhr River, Germany	10–130 ng/L	[93]
		Oderbruch, Germany	71–312 ng/L	[49]
		Oderbruch, Frankfurt, Hessian Ried, Mosel River, Germany	<3–141 ng/L	[94]
		Volcanic lakes, Lazio area, Italy	4–64 ng/L	[66]
		Influent, Sewage water, Spain	0.05–0.30 ng/L	[14]
		Effluent, Sewage water, Spain	0.12–0.70 ng/L	[14]
		Influent, Wastewater treatment plant, Germany	180–260 ng/L	[54]
		Effluent, Wastewater treatment plant, Germany	350–370 ng/L	[54]
		Influent, Wastewater treatment facilities, Sweden	0.09–1.0 μg/L	[69]
		Effluent, Wastewater treatment facilities, Sweden	0.35–0.89 μg/L	[69]
		Osaka North Port sea-based solid waste disposal site, raw water	0.04–87.38 μg/L	[70]
	TCPP	Urban storm water holding tank (SWHT)	410–1,848 ng/L	[65]
		Danube, Liesig and Schwechat Rivers, Austria	33–170 ng/L	[68]
		Ruhr River, Germany	50–150 ng/L	[93]
		Volcanic lakes, Lazio area, Italy	2–62 ng/L	[66]
		Oderbruch, Frankfurt, Hessian Ried, Mosel River, Germany	<4–191 ng/L	[94]
		Influent, Wastewater treatment plant, Germany	650–2,500 ng/L	[54]
		Effluent, Wastewater treatment plant, Germany	820–2,600 ng/L	[54]
		Influent, Wastewater treatment facilities, Sweden	1.1–18 μg/L	[69]
		Effluent, Wastewater treatment facilities, Sweden	3.1–30 μg/L	[69]
		Influent, Sewage water, Spain	0.32–0.72 ng/L	[14]
		Effluent, Sewage water, Spain	0.31–0.91 ng/L	[14]

(continued)

Table 4.2 (continued)

Matrix	PFR	Location	Concentration levels	References
	TBEP	Urban storm water holding tank (SWHT)	36–57 ng/L	[65]
		Rhine, Elbe, Main, Oder, Nidda and Schwarzbach Rivers, Germany	103–663 ng/L	[48]
		Oder River, Germany	121–952 ng/L	[49]
		Danube, Liesig and Schwechat Rivers, Austria	24–500 ng/L	[68]
		Ruhr River, Germany	170 ng/L	[93]
		Volcanic lakes, Lazio area, Italy	8–127 ng/L	[66]
		Oderbruch, Germany	154–410 ng/L	[49]
		Oderbruch, Frankfurt, Hessian Ried, Mosel River, Germany	<33 ng/L	[94]
		Influent, Wastewater treatment facilities, Sweden	5.2–35 μg/L	[69]
		Effluent, Wastewater treatment facilities, Sweden	3.1–30 μg/L	[69]
		Influent, Sewage water, Spain	0.99–33.73 ng/L	[14]
		Effluent, Sewage water, Spain	0.11–9.53 ng/L	[14]
		Influent, Wastewater treatment plant, Germany	3,600–4,000 ng/L	[54]
		Effluent, Wastewater treatment plant, Germany	400–540 ng/L	[54]
	TPP	Danube, Liesig and Schwechat Rivers, Austria	<4.4–10 ng/L	[68]
		Ruhr River, Germany	10 ng/L	[93]
		Volcanic lakes, Lazio area, Italy	2–21 ng/L	[66]
		Influent, Wastewater treatment facilities, Sweden	0.076–0.290 μg/L	[69]
		Effluent, Wastewater treatment facilities, Sweden	0.041–0.13 μg/L	[69]
		Influent, Wastewater treatment plant, Germany	81–93 ng/L	[54]
		Effluent, Wastewater treatment plant, Germany	20–36 ng/L	[54]
		Influent, Sewage water, Spain	0.28–0.47 ng/L	[14]
		Effluent, Sewage water, Spain	0.22 ng/L	[14]
Sediment	TCEP	Osaka North Port sea-based solid waste disposal site	64–7,395 μg/kg dwt	[70]
		River Ems, Germany	0.5–38 μg/kg dwt	[52]
		Danube, Liesig and Schwechat River sediments, Austria	7.7–160 μg/kg dwt	[68]

(continued)

Table 4.2 (continued)

Matrix	PFR	Location	Concentration levels	References
	TCPP	Osaka North Port sea-based solid waste disposal site	2–1,181 μg/kg dwt	[70]
		River Ems, Germany	0.6–226 μg/kg dwt	[52]
		Danube, Liesig and Schwechat River sediments, Austria	0.61–1,300 μg/kg dwt	[68]
	TPP	Osaka North Port sea-based solid waste disposal site	9–130 μg/kg dwt	[70]
		Danube, Liesig and Schwechat River sediments, Austria	0.79–1,300 μg/kg dwt	[68]

for chlorinated PFRs as well as for TCP. TPP, diphenylcresylphosphate (DCP) and TCP were considered to be toxic to (aquatic) organisms. Due to the low values of bioconcentration factors (BCF), chlorinated PFRs do not meet the bioaccumulation criterion [9–11].

4.8 Phosphorus Flame Retardants in Thermoplastic Blends and Nanocomposites

Thermoplastic blends and polymer nanocomposites are a new class of flame retardant additives that work only in the condensed phase and have been developed in the recent years in order to meet flammability standards of materials and improve their properties. According to international standards, the plastic materials used for housings, in transportation area and in electronic devices usually should meet high fires safety standards such as UL 94 V or similar flame retardant specification. The polymer resins have to comply with the RoHS18 and WEEE19 directives. In general, it is not possible to meet these requirements with the pure polymer resins. Therefore, flame retardants are added to the polymer compound. Halogen-free phosphates based flame retardants are of growing importance in electronic enclosures segment, because the electronics industry tends to move to more sustainable flame retardants. In addition to the required level of fire safety, the used polymer resins have to meet additional criteria such as process ability, thermal stability, mechanical properties, hydrolytic stability and recyclability. The combination of requirements can be fulfilled by using phosphorus based flame retardants, especially the aromatic phosphate esters.

Thermosets are, due to the irreversible curing reaction, rigid, three dimensional cross linked plastics. As a result of their three dimensional cross-linked structure, thermosets do not soften or flow when burning. Composites based on thermoset resins like unsaturated polyesters or epoxies are used to a wide extent in the transportation area. Modern railways have to be lighter and more environmentally friendly, and the furnishing of coaches should be not easily ignited and have a low total emission of heat, smoke and toxic fume when exposed to an ignition source. Non-halogen, phosphorus-containing flame retardants are shown to be very effective in thermoset resins. Their advantages lie in their high effectiveness, which enables very low concentrations to be used, while at the same time meeting the most stringent requirements. The low density of the composites makes them useful for all mass transport applications. The phosphorus compounds do not affect the curing reactions of the resins and can be used in cold and hot cured systems. Important thermoset resins are unsaturated polyester resins, epoxy resins, urea and melamine resins, phenolic resins and polyurethanes. The majority of unsaturated polyester resins are reinforced with glass fibers and are used in the building industry, e.g. for facade elements, in the transportation sector, in the electrical industry, e.g. for cable distribution cupboards, for boats and ship building, tanks, tubes, vessels and others.

Usage of flame-retardant polycarbonate/acrylonitrile butadiene styrene (PC/ABS) for monitors and other electronic applications was growing up for more than 12 % at a yearly growth rate from 1990 to 1998. The main reason for this significant growth has been the successful use of non-halogenated flame retardants, especially phosphate esters in PC/ABS blends, providing good properties and acceptable cost to commercially viable systems. All phosphate esters significantly lower the heat distortion temperature and impact properties of PC/ABS while increasing melt flow in so called antiplasticization process.

The use of (alkyl-substituted) triaryl phosphates such as triphenyl phosphate, cresyl diphenyl phosphate, isopropylphenyl diphenyl phosphate, tert-butylphenyl diphenyl phosphate or tricresyl phosphate is very limited in plastics engineering because of their high volatility and relatively low fire retardant efficiency. For instance, the incorporation of TPP in PC/ABS blends [37] does not affect the thermal decomposition behavior of the blend. In fact, TPP volatilizes before decomposition of the polymer blend, causing polycarbonate to stress crack. However, TPP with a phosphorus level of around 9 % is a very efficient flame retardant, and its being a solid offers ease of handling in a variety of compounding environments. Depending on the ratio of polycarbonate to ABS, levels of 8–10 % of TPP are needed to achieve a UL-94 V-0 rating at 1/16 in.

The next generation of phosphate esters developed for PC/ABS were bisphosphates in an effort to increase molecular weight, and therefore decrease volatility and mobility/juicing to the surface of the plastic part. Resorcinol diphosphate was the first material developed for PC/ABS and it is a liquid additive with 9 % P content and good efficacy as a flame retardant. Bisphenol A bisphosphate is another liquid with properties similar to RDP. It is more viscous than RDP and needs to be heated in order to be metered into the extruder. Stress cracking is better with BADP, probably because of the compatibility of the additive in the polycarbonate matrix. Thermoset matrix resins can be based on epoxy, unsaturated polyester, or phenolic chemistries. The resins are usually prepared in two stages, an initially low-molecular weight oligomer liquid and then its curing during subsequent processing. Reactive strategies for achieving flame retardancy are often employed for thermosets in either the first or the second stage of their preparation. Ammonium polyphosphate and red phosphorus are excellent halogen-free flame retardants for all types of thermoset resins. In the most cases, the combination of red phosphorus with aluminum hydroxide passes high levels of flame retardancy at relatively low amounts of fillers. The low filler levels reduce the viscosity of the formulations and the density of the laminates.

Polyurethane casting resins require in many cases the addition of flame retardants. The addition of red phosphorus and aluminium hydroxide is much more effective and does not affect the insulating properties of the resins. Such low filled formulations can be used in each application, where low viscosity resins are required. Incorporation of stabilizers could retard these reactive processes. One of the first such proposed stabilizers consisted of silicon oil or a combination of ammonium bisulfate, paraffin oil, and pentaerythritol [75]. These stabilizers were blended with red phosphorus powders before mechanical incorporation into the polymer composition. As the application of red phosphorus migrated to epoxy, other methods to ensure more stable red phosphorus were developed. The principal approach consisted of coating red phosphorus particles with a thermosetting resin, such as formaldehyde-based, melamine-based or phenol-based compositions [76–78]. Thermosetting resin coatings provided a number of advantages, including improved coverage, superior wett ability and increased resistance of the melt-proof coatings to industrial processes. The primary coating process consisted of adding the thermoset resin, as a raw material or a precondensation product, to an aqueous dispersion of red phosphorus particles. The mixture was agitated and then polymerized. Upon the coating treatment, a dispersion stabilizer and a stabilizer for red phosphorus such as magnesium hydroxide may be added to the aqueous dispersion. After the polymerization procedure, the treated red phosphorus particles were filtered, washed with water and dried. Additional stabilization methods included the use of aluminium hydroxide ($Al(OH)_3$) [79]. These methods noticeably reduced the formation of phosphine and of phosphorus oxygen-containing acids, but were not considered completely sufficient. Additional improvements in making red phosphorus safe and efficacious were initiated through the development of a dual coating process, consisting of an initial coat of aluminium hydroxide and/or zinc hydroxide, followed by an additional coat of thermoset resin. The initial coat was applied by mixing red phosphorus powder with aluminum sulfate in an aqueous solution. The composition is adjusted to a pH value of approximately 8–9 so that $Al(OH)_3$ precipitates on the individual particles of the red phosphorus powder. The second coat is applied when the encapsulated powder is dispersed into an aqueous solution of ammonium chloride and a pre-condensed resin. The resin then precipitates on the pre-encapsulated red phosphorus particles when the temperature of the solution is increased to approximately 100 °C.

Dual coating method can’t meet the requirements for resinous materials intended to use in high performance electronic components in which an extremely high resistance to moisture and corrosion is required, so pulverization process is required. These improvements in red phosphorus led to their incorporation into plastic encapsulants for integrated circuits (IC’s). This application required that the flame retardant chemistry be very stable over long periods of time when exposed to humidity and elevated temperatures.

The red phosphorus-based flame-retardant was coated with a primary coat of aluminum hydroxide and a secondary coat of phenol resin. The content of red phosphorus in the coated flame-retardant is preferably 60–95 % by weight. When the red phosphorus content is less than 60 % by weight, it becomes necessary to incorporate a large amount of the flame-retardant into the epoxy resin composition and the addition of a large amount of the flame-retardant decreases the moisture resistance of the encapsulant. When the content of red phosphorus exceeds 95 % by weight based on the weight of the flame-retardant, there is a problem in respect to the stability of the red phosphorus.

Epoxies have satisfactory mechanical properties such as suitable weather, chemical and thermal resistance. Epoxies are applied for molding compounds, surface coating and painting materials, composites, microelectronic encapsulated materials, printed circuit boards, adhesives, etc. Affectivity of PFR depends on the chemical structure of the polymer, they are particularly effective in materials with high oxygen content, like polyesters, polyurethanes, epoxies or cellulose. PFR is converted by thermal decomposition to phosphoric acid. Further thermal decomposition leads to the formation of polyphosphoric acid. The polyphosphoric acid esterifies and dehydrates the pyrolysing polymer. Unsaturated compounds are formed with subsequent charring. The carbonization process occurs via several steps. The non-volatile, polymeric phosphoric acids inhibit further pyrolysis reactions by providing the simultaneously forming carbonaceous layer with a glassy coating. This protective layer is resistant to even higher temperatures and shields the underlying polymer from attack by oxygen and radiant heat. In addition to polyphosphoric acid being formed also reducing compounds such as phosphites can be present. They reduce carbon oxidation in favor of char.

Flame retarded epoxy resins for printed circuit boards are produced by reacting tetrabrom-bisphenol A into the liquid resins. To comply with the flame retardancy specification UL 94 V-0, the resins contain about 20 % bromine. In case of fire or smoldering, brominated epoxies evolve highly corrosive decomposition products that can damage the surrounding electronic equipment. This is not the case when PFRs are used [80]. Flame retardancy of printed circuit boards can be attained by the addition of finely divided red phosphorus. The thermal and electrical properties of the laminates are not affected by the incorporation of red phosphorus.

In the few cases where phenolic resins require fire retardant treatment (e.g. paper composites), reactive flame retardants like tetrabrombisphenol A or additive flame retardants like organophosphorus compounds are used. Ammonium polyphosphate is also an effective flame retardant in phenolic resins.

Nanocomposites constitute a relatively new development in the area of flame retardancy and can offer significant advantages compared to traditional approaches. Composites in general are structures formed from two or more physically and chemically distinct phases, and the inherent understanding is that their properties are superior to those of the individual components. The component phase morphologies and interfacial properties influence the structure and properties of the composite. Nanocomposites are based on the same principle as conventionally filled polymers, but nanometer scale of mixing makes their properties superior to conventionally filled polymers.

The most common nanocomposites are polymer layered silicate structures. Blumstein in 1961 was the first to report in the literature nanocomposite structures and in 1965 demonstrated the improved thermal stability of PMMA-layered silicate nanocomposite. The real commercial interest in the technology of nanocomposite structures did not occur until the 1990s. In the past two decades, many researchers have paid attention to polymer/layered-silicate nanocomposites (PLSs), especially to polymer/organically modified clay (organoclay) nanocomposites. These PLS materials often exhibit remarkable improvement in properties over those of both virgin polymer and conventional filled systems, and many represent a better choice than the latter system. Therefore, nanotechnology has been described as the next great frontier of materials research because nanocomposite formation brings about improved material performance, including enhanced mechanical, thermal, optical, dimensional, and barrier performance properties [81, 82]. Key advantages of nanocomposite structures are high modulus and strength, high heat distortion temperature, low gas permeability, improved solvent resistance, and thermal stability. The polymer structures based on nanocomposites significantly improve the thermal stability and self-extinguishing characteristics of the polymer matrix where they are incorporated. Conventional compounding techniques such as extrusion and casting can be used to fabricate nanocomposites; this makes them very attractive from a cost/performance perspective compared to the traditional composite manufacturing methods. Applications in film and fibers are also possible where they would be prohibited with traditional microscale composites.

There are two classes of silicates used in nanocomposites: layered silicates (clay minerals) and phyllosilicates (rock minerals). Clay minerals consist of two structural units: a sheet of silica tetrahedral and two layers of closely packed oxygen or hydroxyl groups in which aluminum, iron, or magnesium atoms are embedded so that each is at the same distance from six oxygens or hydroxyls. The silica tetra hedra are arranged as a hexagonal network where the tips of the tetrahedra all point in the same direction. The same structure of silica tetrahedra is found in phyllosilicates.

The most important structures of polymer nanocomposite materials are the following:

- Intercalated structures: the monomer or the polymer is sandwiched between silicate layers. The clay layers maintain registry in the system.
- Delaminated or exfoliated: the clay layers have lost registry. The exfoliated structure can be ordered (silicate layers are unidirectional) or disordered (random dispersion of silicate layers).
- End-tethered structure: one layer of the silicate or the whole silicate is attached to the end of the polymer chain.

For optimum physical properties, exfoliated structures are better than intercalated ones. However, for flame retardancy, intercalated structures could be adequate to modify the pyrolysis mechanism and induce a solid-phase mechanism of ignition resistance.

Nanocomposites are not formed by the simple mixture and physical proximity of a polymer and a silicate. Exfoliation could only be achieved in polymers containing polar functional groups such as amides and imides. This is expected because the clay silicate layers have polar hydroxy groups that can interact only with polymers containing polar functional groups.

This is where ion exchange reactions are critical in rendering the silicate surface organophilic and facilitating interaction with a wider class of polymer matrices. Alkyl ammonium cations are normally used to achieve an efficient ion exchange. Generally, a polymer–organoclay with flame retardant additives may be prepared either by a blending process through melt or solution blending, or by an in situ polymerization process, depending on starting materials and processing techniques.

In the solution blending method, the organoclay is first swollen in a solvent. Then a flame retardant additive and polymer are added to the organoclay solution. The polymer dissolves in the solution, and the polymer molecule chain can intercalate into the gallery of the organoclay. Upon solvent removal, a nanocomposite is obtained. The solvent must be compatible with polymer, organoclay, and flame retardant additives. It can be difficult to select an appropriate solvent for this method. Therefore, solution blending is not often used to prepare flame retardant nanocomposites.

In the melt-blending method, the flame retardant polymer–organoclay nanocomposites are prepared by mixing the flame retardant additive, the organoclay, and the polymer at above the softening or melting point of the polymer through mechanical mixing and shearing introduced by an internal mixer or twin-screw extruder. Generally, organic modification of the clay can be achieved prior to the nanocomposite preparation. However, it can also be achieved by adding both pristine clay and surfactant to the flame retardant polymer formulation during melt blending, thus eliminating some preparation steps. This method is environmentally benign, due to the absence of organic solvents, is compatible with current industrial processing, and provides a potentially economical and convenient way of imparting and promoting superior flame retardancy for commercial polymers. Polystyrene, polyamides, polyesters, polycarbonate, polyphosphazene, and polysiloxane nanonocomposites can be prepared by this method. Flame retardant polyamide-6 (PA6)/organoclay nanocomposite was prepared by blending PA6, OMT, and magnesium hydroxide–red phosphorus (MH–RP) using a twin-screw extruder to obtain PA6/OMT/MH–RP nanocomposite [83, 84]. Morphology of melt-blended nanocomposite could be analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). d-spacing of the OMT increases after organic modification by hexadecyltrimethylammonium bromide (C16) from 1.3 to 2.2 nm. Upon formation of the ABS–OMT and PA6–OMT nanocomposites, the d-spacing increases further, from 2.2 to 3.1 and 3.3 nm, respectively, and the diffuse diffraction peak for the nanocomposite indicates the formation of an intercalated–exfoliated morphology. The addition of flame retardant additive, MH–RP, in the nanocomposite formulation during melt blending has a minimal effect on the position and shape of the (001) plane diffraction peaks, and therefore no further exfoliation occurs.

The generally accepted opinion is that both exfoliated and intercalated morphologies impart measurable improvement in both mechanical and flame retardant properties, but the exfoliated morphology imparts greater improvement in mechanical properties than does the intercalated morphology. There does not appear to be a significant difference between the intercalated and exfoliated morphologies in flame retardant performance for polymer nanocomposites. When both intercalated and exfoliated morphologies exist in a polymer matrix, increasing the exfoliation level probably benefits the improvement of the mechanical properties for polymer nanocomposites. The exfoliated morphology formation depends on the nature and interactions between the surfactant, the clay, and the polymer matrix. Until now, the relationship between the morphology and properties of the polymer–organoclay nanocomposites has not been completely revealed, but with further research and development on the nanocomposites, this may be resolved.

Kim et al. [85] reported different melting blend method from those mentioned above. First, a mixture of triphenyl phosphate and organoclay was mixed to obtain nano TPP. Then an epoxy resin and silane-coupling agent were added to the mixture to obtain the final flame retardant mixture. Finally, this mixture and ABS was blended in a Haake Plasti-Corder mixer to obtain the flame retardant ABS–OMT–TPP nanocomposites. The epoxy resin and silane coupling agent act as flame retardant synergists. XRD analysis shows that the d-spacing of organoclay increases by intercalation of TPP. The intercalated TPP can escape from nano TPP upon heating to 300 °C; there is no chemical bond between TPP and clay. However, the intercalation of TPP into the gallery space of the organoclay could reduce the volatility and suppress the evaporation rate of TPP. Alkyl-substituted triaryl phosphates such as cresyldiphenyl phosphate, isopropylphenyldiphenyl phosphate, tert-butylphenyldiphenyl phosphate, tricresyl phosphate, and trixylyl phosphate have very limited application in engineering plastics because of their high volatility and relatively low flame retardancy. The organoclay can probably be used to increase the thermal stability and flame retardant properties of these aromatic phosphates by forming an intercalated ArP–organoclay hybrid.

Polymerization as preparation method for polymer–organoclay involves dispersing the clay in the monomer and carrying the polymerization reaction around it. Polystyrene clay nanocomposites can be prepared by polymerizing styrene in the presence of clay. Exfoliation of layered silicates in Nylon 6 greatly improves the thermal, mechanical, and barrier properties of the polymer. The Nylon 6 layered silicate nanocomposites containing 5 % of nanoclay by weight exhibited increases in tensile strength by 40 %, in tensile modulus by 68 %, in flexural strength by 60 %, and in flex modulus by 126 %. The heat distortion temperature exhibited an increase from 65 to 152 °C.

FR mechanism of flame retardancy in nanocomposite containing polymers is a consequence of high-performance carbonaceous-silicate char build up on the surface during combustion. During pyrolysis, the nanocomposite structure collapses and the resulting carbonaceous-silicate structure forms a char layer. This layer acts as a thermal barrier, keeping the heat source from reaching the polymer surface, and as a barrier to diffusion of combustible decomposition products into the gas phase. Recent experiments [86] have revealed that the carbon vanishes and the clay accumulates on the surface of a degrading polymer. Residue yields do not improve with nanocomposites; therefore the mechanism of action is not that of retention of the char in the condensed phase.

Gilman et al. [87] studied the effect of an exfoliated versus an intercalated structure on flame retardancy and concluded that no universal optimum exists: for certain polymers, an intercalated structure is best (epoxy and vinyl esters); for others (polystyrene), the exfoliated structure achieves better flame-retarding performance. Processing conditions also affected the flame-retarding efficacy of the polystyrene nanocomposite. Both solvent mixing in toluene and extruder melt blending (170 °C under nitrogen or vacuum) produced structures with reduced flammability. However, inclusion of air or high extrusion temperatures affected flammability negatively, resulting in a nanocomposite with no improved flammability over the base formulation.

Efforts to modify traditional flame retardants with the nanocomposite technology are documented in the work of Lomakin et al. [88] and Ruban et al. [89], who studied PVA, polystyrene, and Nylon 6 with modified TPP. TPP, an effective flame retardant on its own, was intercalated using kaolin, and its effectiveness increased. TPP has been shown to traditionally work in the gas phase, releasing P*, which acts as a radical trap in the gas phase. When TPP is intercalated, the mechanism of degradation of TPP changes to the condensed phase. Char formation is present in intercalated TPP, but is absent in TPP-only combustions. This is an evidence of cross-linking and aromatic reactions.

4.9 Future Trends

Polymer–clay nanocomposites have attracted a great deal of interest due to their improved mechanical, thermal and biodegradability properties. Furthermore, an improvement in the flammability properties of polymers has been achieved with polymer–clay nanocomposites, which could provide an alternative to conventional flame retardants (FR). However, the relationship between the morphology and properties of the polymer–organoclay nanocomposites has not been completely revealed, but with further research and development on the nanocomposites, this may be resolved.

Special attention should be focused on the potential environmental impact of the production and use of thermoplastic blends and nanocomposites and they should also be assessed holistically from cradle to grave (i.e. including the treatment or disposal of the material at the end of its useful life). The steps involved in separating different polymers (or polymer/additive blends) and organoclay nanocomposites within waste streams, in order to allow them to be recycled, are not a trivial task.

Bio-sourced polysaccharide structures, derived from natural starch derivatives, can provide a green component of flame retardant systems. Nano "sponge" structures produced from cyclodextrins (cyclic oligosaccharides—long sugar molecules configured into structures of linked, large rings) have been tested with flame retardants ammonium polyphosphate and triethylphopshate. APP offers not only a positive health and environmental safety profile, but also the advantage of providing both phosphorus (acid release) and ammonia (blowing agent) for effective char production and so fire protection. The PFRs can be enclosed in the nano sugar sponge structure, improving mixing with plastic polymers, so enabling high flame retardant loadings without deteriorating polymer mechanical performance. Fire performance tests using the nano sugar sponge—PFR combination (heat release, heat of combustion, mass loss, smoke) showed that the combination was effective for polypropylene, linear low density polyethylene and polyamide 6 [90]. Thus, those environmentally friendly structures should be introduced in market products.

Further studies should be also focused on the PFRs-degrading bacteria, and on the detoxification techniques, could help to establish more efficient detoxifications, and could also provide novel insights into microbial degradation of currently non investigated degradation processes for PFRs. The bacteria and the microbial detoxification techniques may prove useful for the bioremediation of sites contaminated with intractable compounds.

4.10 Conclusion

This chapter describes the main physico-chemical properties, occurrence and determination in the environment of phosphorus containing flame retardants as well as their applications in commercial products and new perspectives of their usage in thermoplastic blends and nanocomposites. Flame retardants are selected based upon polymer chemistry and fire physics, regulatory tests according to flame retardant response needs, flame spread, ignition resistance, smoke/gas release, etc. Special attention is focused to polymer chemistry, regulatory test needs, commercial requirements, and environmental needs essential to successful electronic equipment flame retardant material development. FR should be environmentally friendly compounds or eventually be recycled or used for waste-to-energy recovery.

Although halogenated flame retardants are used widely, in particular for polymers composites or in materials for electronics, they can cause dangerous effects. They may give rise to toxic, acidic, and dense smoke which can threaten people and damage costly equipment. Hence, the use of brominated flame retardants (BFRs) has been prohibited because highly toxic and potentially carcinogenic brominated furans and dioxins may form during combustion. As a result of the growing concern regarding the adverse effects inherent during thermal degradation in the halogenated additives used currently, a significant amount of research has been devoted to the development of non halogenated additives for flame retardant polymer formulations.

PFRs haven been used as FR because of their different or complementary use and function compared BFRs and because the use of the latter are restricted more and more. Phosphorus compounds have some advantages compared to BFRs. According to the available environmental and toxicity data, no problems are expected when replacing BFRs by RDP, BADP, or melamine polyphosphate. Only the Cl-containing PFRs are proven to be carcinogenic, and severe negative human health effects were found for Cl-containing PFRs as well as for TCP, which makes those PFRs unsuitable as alternatives for BFRs. TPhP, DCP and TCEP would also not be suitable alternatives for BFRs, because they are considered to be toxic to (aquatic) organisms and/or (potential) carcinogenic. Diethylphosphinic acid is, just like TCEP, considered to be very persistent, which does not make diethylphosphinic acid a proper substitute for BFRs either. In conclusion, based on the currently available environmental and toxicity data, RDP, BADP and melamine polyphosphate may be considered as suitable substitutes for BFRs, but TPhP, DCP, diethylphosphinic acid, TCP, TCPP and TCEP are not recommended as alternatives for BFRs.

Organically treated layered silicates (so called organoclays), carbon nanotubes/nanofibers, or other submicron particles at low loadings (1–10 wt%) have been recently developed according to the market and fire safety requirements, however they are upon research and have not been yet included in market as commercial products. Polymer nanocomposites greatly lower the base flammability of a material, making it easier to flame retard the polymer containing a nanocomposite structure. They are effective when combined with all types of FR additives. Polymer nanocomposites bring balance of mechanical and flammability properties to a system, tend to inhibit polymer dripping/flow under fire conditions, they provide no great cost increase since very little additive is needed and also they have multifunctional performance (i.e. electrical conductivity from carbon nanotubes). Nanocomposite polymers offer improved stiffness without loss of impact strength, improved heat distortion temperature, improved transparency, improved barrier characteristics and improved flame retardancy because of the formation of a three-dimensional inorganic network. At the other site, it is very difficult to set up a polymer nanocomposite structure, nanocomposites require careful design and analysis, which can bring additional cost to a product. Also, there are lots of unknowns with nanocomposite technology (long-term aging, etc.) since it is a new technology, introduced in 1990s and probably not proven enough for conservative fire safety principles.

In summary, flame retardant polymer–organoclay nanocomposites can be prepared using melt blending, solution blending, or the in situ polymerization method. Intercalated, exfoliated, or intercalated–exfoliated morphology is formed in the polymer matrix. Addition of flame retardant additives hardly affects nanocomposite formation. Specifically, flame retardant additives are introduced into the polymer nanocomposite formulation by three approaches:

1. A flame retardant additive can be added during nanocomposite preparation. Generally, both inorganic and organic flame retardant additives can be added to the formulation by this approach; and their presence is not expected to affect the nanocomposite morphology.

2. Flame retardant additives are incorporated into the organoclay through ion exchange or physical adsorption before nanocomposite preparation.
3. An organic group or oligomer containing flame retardant elements such as bromine or phosphorus can be grafted to the surfactant used to modify the clay.

The miscibility between flame retardant additives and the polymer matrix in a flame retardant formulation restricts the properties of the flame retardant polymer. Poor miscibility between flame retardant additives and the polymer matrix often causes a decrease in the mechanical and other properties of the base polymer used in a flame retardant formulation. However, the addition of organoclay may bring about simultaneous improvement in the flame retardant and mechanical properties, thereby offsetting any adverse effects imparted by the flame retardant additives. Moreover, the latter two approaches both impart a flame retardant performance to organoclay by incorporating the flame retardant additive into the gallery space of the organoclay. When the organoclay is nano-dispersed, the flame retardant additives will also be well dispersed in the polymer matrix during nanocomposite preparation, which facilitates dispersion of the flame retardant additives in the polymer nanocomposite. Moreover, addition of the organoclay may lead to a significant reduction in the amount of the flame retardant needed, while maintaining or even improving the flammability performance and physical properties of the flame retardant polymer. Electronic enclosures are a market segment which includes primarily the enclosures of consumer and information technology equipment such as televisions, desktop or notebook computers, monitors, printers, copiers, household appliances, etc. These housings are made of different types of polymer resins such as high impact polystyrene (HIPS), acrylonitrile butadiene styrene copolymers (ABS), polycarbonate/ABS blends (PC/ABS) and polyphenylene ether/HIPS blends (PPE/HIPS). So the usage of organoclay nanocomposites in electronic equipment could be very useful.

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Chapter 5
A Review of Non-halogen Flame Retardants in Epoxy-Based Composites and Nanocomposites: Flame Retardancy and Rheological Properties

Seongchan Pack

Abstract Since more environmental regulations restricted to the use of halogen-based flame retardants are issued the halogen-free flame retardants have been gradually increased in demand at electronics applications. Several DOPO derivatives and recently developed phosphorus containing flame retardants are introduced into the market as a counterpart of tetrabromobisphenol A (TBBA). This short review paper focuses on their flame retardancy and material properties in epoxy resins. The inclusions of inorgano-metallic compounds and nanoparticles are also briefly reviewed for their potential opportunities in the epoxy composites.

Keywords Non-halogen flame retardants · DOPO derivatives · Epoxy-based composites · Nanocomposites · Nanoparticles

5.1 Introduction

For several decades, polymeric materials are extensively used in a variety of applications, such as consumer appliances, construction and transportation applications, and electrical/electronic devices because they are sustainable, lightweight and cost-effective [1, 2]. In particular, epoxy resins are one of well-known thermosetting polymers and used for coating and adhesive applications, which can also be reinforced with fibers or additives for obtaining high strengths and good chemical resistances [1–4]. It is reported that almost 65 % of glass-fiber reinforced composites have been consumed at the sectors of transport and construction [3]. However, they are intrinsically combustible and needed flame retarded [3, 4].

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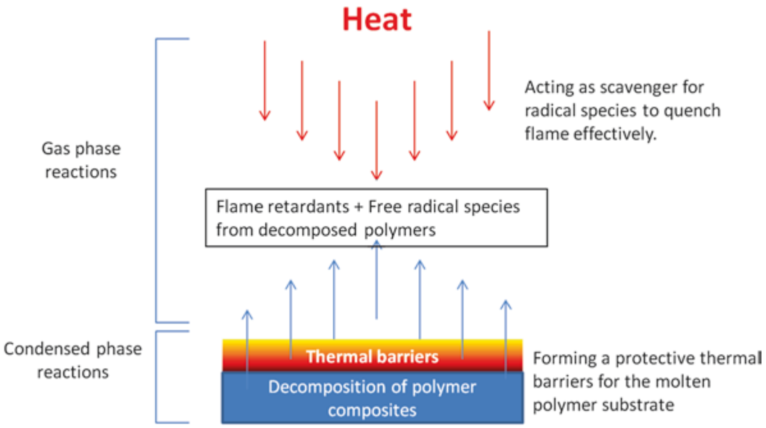
It generally is believed that a degree of the flammability of epoxy resins depends on epoxy monomers and curing agents, where the epoxides containing aromatic groups produce more char formation when it is exposed to a heat source [5, 6]. Although the cured epoxy resins have some degree of flame retardancy itself, it is not enough to pass a stringent industrial standard flammable test, such as UL-94 V0. Thus, the addition of flame retardants is one of practical means to improve the flame retardancy of epoxy resins system.

The majority of flame retardants for epoxy resins are currently halogen-based flame retardants because their flame retardancy is very effective at gas phase and cost-effective at an industrial scale. Tetrabromobisphenol A (TBBA) is the leading halogenated flame retardant in epoxy resins system for electrical and electronic devices since it has good thermal stability and flammability as well as high Tg when it is formulated with curing agents [3]. However, since environmental concerns using the halogenated flame retardant arose from the daily consumer products, the two major brominated flame retardants, pentabromodiphenyl ether (PBDE) and octabromodiphenyl ether (OBDE) have recently been phased out in North America and European markets, which could release toxic gases and may be even accumulated in a living organisms for a long period time [7].

Due to the environmental issues mentioned in the previous paragraph, TBBA would be also eliminated in epoxy and reinforced epoxy markets near future [3, 6]. Thus, new approaches for the developments of non-halogenated flame retardants have been initialized and flourished at both academics and industries. In this short review, we first describe the mechanism of non-halogen flame retardants and then review current developments of phosphorus-containing flame retardants for epoxy resins. In particular, cured epoxy composites system with different epoxy resins and curing agents are extensively reviewed in terms of their flammability and rheological/mechanical properties. Later on, a current development using inorgano-metalic compounds and nanofillers is reviewed in epoxy composites containing non-halogen flame retardants.

5.2 The Mechanism of Flame Retardant Materials in Epoxy-Based Composites

The combustion of polymeric materials is a complex processes involved with a series of heat and mass transfer at the surfaces of polymer melts so that an intervention of the combustion processes can be achieved by the addition of flame retardants (FRs) which makes the polymers less combustible [3]. FRs materials generally react at either gas phase or condensed phase. It depends on what types of FRs materials. In case of halogen-based FRs, the hydrogen halides are formed from the FRs decomposition, which subsequently reacts with free-radical species from decomposed polymers at gas phases [4–6]. On the other hands, in case of non-halogen-based FRs, the thermal insulation processes mainly occurs at condensed phases. For example, phosphorus-based FRs release PO_2 or PO_3 at gas phase and then is oxidized to P_2O_5. A formation of the phosphoric acids can result



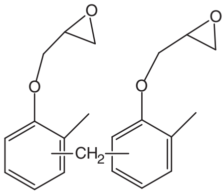
Scheme 5.1 A series of flame retardant reactions with polymers occurs at condensed and gas phases

in intumescing chars formation at the polymer surfaces, which acts as thermally protective layers on polymer-melts against heat front. These charring processes eventually interrupt the combustion processes [7, 8]. A mechanism of flame retardants in polymer composites is shown in Scheme 5.1.

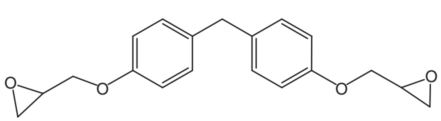
Epoxy-based composites formulated with TBBA and DDS as curing agent are flame-retarded in the decomposition steps: the halogen halides from TBBA are first released at above 300 °C and then the nitrogen element from DDS exists in a form of cross-linked structures in its residues [9]. In contrast, the epoxy resins containing phosphorus-based flame retardants mainly decomposes at the condense phase in which P-rich residues are found at the end of combustion. This result may be explained by the existence of element P, which can act as a catalyst for promoting chars formation [10].

5.3 Review of Reactive Phosphorus-Based Flame Retardant Epoxy Resins System

In epoxy resins formulation, phosphorus-containing flame retardants can be applied as an additive, which is relatively easy to manufacturing process. However, it has some technical drawbacks, such as particle dispersion and deterioration of the physical properties of epoxy laminates when its loading is too high [5]. Thus, molecularly reactive phosphorus-containing flame retardants have been used for advanced epoxy laminates, which can give better performance on flame retardancy and material properties. The common epoxy resins are either *o*-cresol formaldehyde novolac (CNE) or diglycidyl either of bisphenol-A (DGEBA), which are frequently pre-reacted with non-halogen flame retardants in order to improve flame retardancy of the cured epoxy resins.

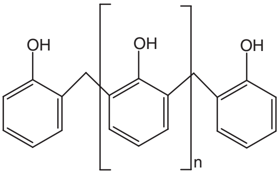


O-cresol formaldehyde novolac (CNE)

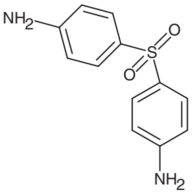


Diglycidyl either of bisphenol-A (DGEBA).

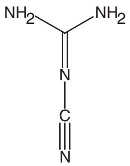
The majority of non-halogen flame retardants that pre-reacted with the epoxy resins are based on 9,10-dihydro-9-oxa-10-phosphaphenanthren 10-oxide (DOPO, I), which is shown in Fig. 5.1. Because of its intrinsically high reactive properties the addition of DOPO can impart good flame retardancy to epoxy laminates applications [5, 11]. Moreover, a combination of the DOPO with curing agents often help reducing the amount of % P that required for UL94-V0, which may result in obtaining an improvement on the materials properties of cured epoxy systems, such as phase transition temperature, thermal stability and modulus. They can also improved by different curing agents systems, such as phenolic novolac (PN) and 4,4-diaminodiphenylsulfone (DDS).



Phenolic novolac (PN)



4,4-diaminodiphenylsulfone (DDS)



Dicyandiamide (DICY)

Thus, a variety of phosphorus-based flame retardants have been developed and studied for their flammability as well as rheological and mechanical properties. Recently, the two review papers extensively focused on the flame retardancy of

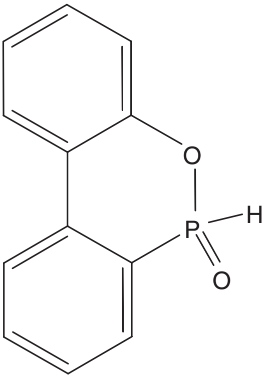


Fig. 5.1 9,10-dihydro-9-oxa-10-phosphaphenanthren 10-oxide (DOPO), I

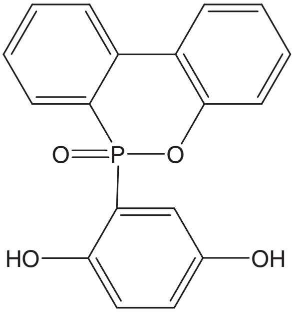
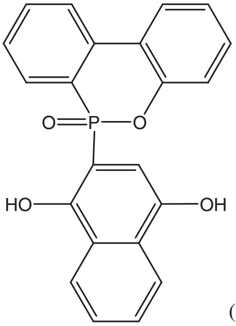
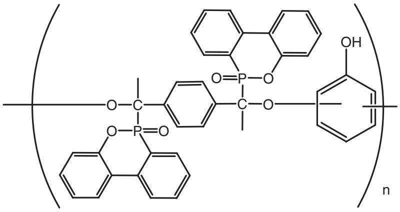
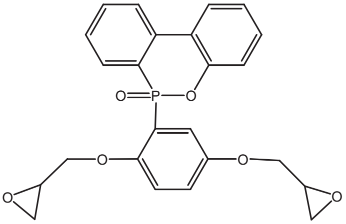
non-halogen flame retardants for epoxy resins system [5, 6]. However, few review papers were found for the rheological and mechanical properties of epoxy resins with non-halogen flame retardants. In this section, we review not only the flame retardancy of several DOPO derivatives and phosphorus-containing flame retardants but also their rheological and mechanical properties in cured epoxy resins, where a correlation with curing agents and % P content may exist at each epoxy resins system.

5.3.1 DOPO-Derivatives Flame Retardants System

Since the P-H group is highly reactive, it is relatively easy for the DOPO to be synthesized with several functional groups. Wang and Shielh reported that 1,4 benzenediol was synthesized with the DOPO and then evaluated as a curing agent in a CNE epoxy (EEW:192). They showed that the cured CNE epoxy containing 25 % of DOPO derivative (II) and 75 % phenolic navolac (PN) was ranked as UL94-V0 in which the total phosphorus content was 1.1 % [11, 12]. However, 4.4 % P content was required to keep the UL94-V0 when the DOPO derivative was solely used as curing agent. Rwel et al. [13] also showed that a mixture of two curing agent (i.e. DOPO with the 1,4-naphthalenediol(III) and PN) could have the reduced phosphorus content for obtaining higher residues and thermal stability in N_2. Thus, the required % P content for good flame retardancy can be reduced by the combination of DOPO derivatives with conventional curing agents. Introducing phenol groups into the DOPO can improve char formation in epoxy resins. Liu et al. synthesized an alkyl novolac (IV) from a reaction of DOPO with 1,4-benzenedicarboxaldehyde and phenols. The alkyl novolac was used as a co-curing agent with PN in a CNE epoxy resin (EEW:200). Only 3.8 % P content in the cured epoxy could lead to having 55.4 % residues and 32.5 in. LOI [14]. It was interesting that the amount of the residues was highest when the similar level of % P content was found in cured CNE epoxy resins in which different DOPO derivatives (II–IV) was included. This may result from the existence of the hydroxyphenyl groups in the flame retardant backbone.

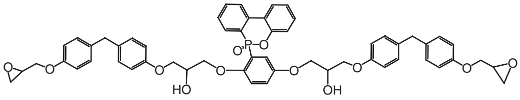
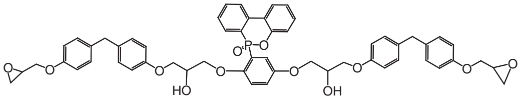
On the other hand, DOPO derivatives are frequently pre-reacted with epoxy groups since it has reported that the incorporation of organophosphorus molecules into epoxy backbones could release less smoke and toxic gases [15, 16]. Wang et al. showed that 2.0–2.8 % P in the pre-reacted DGEBA with the diol flame retardants (II) could give UL94-V0 to the cured epoxy, whereas the DOPO derivative reacted with epoxy groups needed more % P content in order to obtain the same level of UL94 grade [11, 16, 17]. This discrepancy may be explained by the use of different curing agents and epoxy equivalent weights (EEW). Wang et al. showed that the DOPO derivative (II) epoxy resin was cured with the three different curing agents. Both PN and DDS needed ~4.7 %P content for UL94-V0. But, the cured epoxy resin needed to have 7.2 % P content in case of DICY curing agent [15]. He also demonstrated that either DDS or PN could give 30 in LOI when the EEW of DGEBA epoxy resins containing the DOPO derivative (II) was above 300, where the % P content was 1.7 % [17]. Thus, DOPO derivatives can be variable to be used as either co-curing agent or pre-reacted with epoxy resins. The summary of the DOPO derivatives and its flammability are presented in Table 5.1.

Table 5.1 Several DOPO derivatives and their advanced epoxy resins are presented with different curing agents and its flammability

DOPO derivatives/epoxy resin	Epoxy resins or curing agents	% P	UL94 V-0, LOI
 (II)	*o*-Cresol formaldehyde novolac (CNE, EEW:192)	4.4	V-0 [11]
 (III)	*o*-Cresol formaldehyde novolac (CNE, EEW:195)	4.1	31 [13]
 (IV)	*o*-Cresol formaldehyde novolac (CNE, EEW:200)	3.8	32.5 [14]
 [EEW:223-228]	Phenolic novolac (PN)	4.8	34 and V-0 [15]
	4,4-diaminodi-phenylsulfone (DDS)	4.5	32 and V-0 [15]
	Dicyandiamide (DICY)	7.2	36 and V-0 [15]

(continued)

Table 5.1 (continued)

DOPO derivatives/epoxy resin	Epoxy resins or curing agents	% P	UL94 V-0, LOI
 [EEW:530-550]	4,4-diaminodiphenylsulfone (DDS)	2.4–2.8	32 and V-0 [16, 17]
 [EEW:483]	Methylene dianiline (MDA)	2.1	UL94-V0 [11]

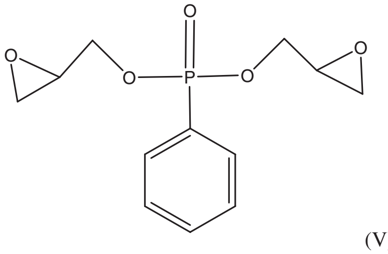
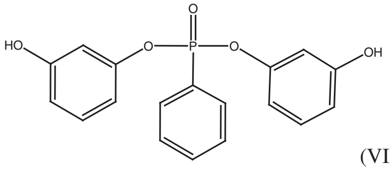
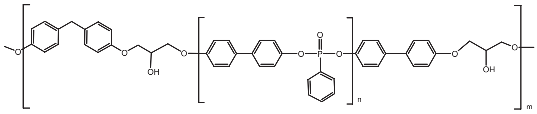
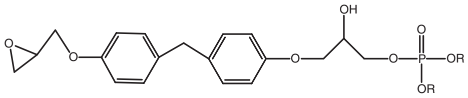
5.3.2 *Phosphorus Containing Flame Retardants System*

Several research groups have reported that organophosphates or organophosphine oxides can be chemically pre-reacted to epoxy resins, which also imparts good flame retardancy to the cured epoxy resins [18–23]. Cheng et al. reported that di-epoxide containing phenyl phosphonate [V] could be cured with DDS having 29–31 in LOI. However, the cured epoxy resin had a lower thermal stability and higher % P content needed to obtain the better flame retardancy [20, 21]. Moreover, the high level of the % phosphorus content may be caused to lower the glass transition temperature (Tg) of the cured epoxy resins. Thus, the % P content in a finial epoxy formulation has to be reduced while other materials properties remain as same. Ren et al. showed [18] that the phenyl phosphine oxide with bis-phenoxyl (VI) was synthesized with the epoxy resins and then cured with DDS in which 34 of LOI and good thermal stability (~357 °C at 5 % weight loss in N_2) were obtained. The % P content was also reduced to 7.8 from 9.5. The concentration of the P content may be still high enough to affect the material properties of the cured epoxy resins. Therefore, the epoxides groups have to be replaced by more thermally stable and cross-linked epoxy resins.

DEGBA is a good cross-linked and relatively produces higher residues because of the bisphenol groups in its backbone. It can be also synthesized with a variety of phosphorus-based flame retardants. Lin et al. reported that the amount of % P was reduced by replacing the bis-phenoxyl with bis-diphenoxyl group in the DEGBA epoxy resin, where only 1.5 % P could be contributed to achieving above 30 in LOI, high Tg (180 °C) and higher residues remained (26 % in N_2) [19]. In the report, the advanced epoxy resins with the phosphorus-based flame retardant [VII] had the highest number of LOI obtained among the epoxy resins with other flame retardants, such as TBBA, DHBP (dihydroxybiphenyl) and PPA (phenyl phosphonic acid).

Organophosphate molecules are also used to increase thermal stability of the cured epoxy resins. Derouet et al. synthesized a series of alkyl or aryl phosphates [VIII] with a DEGBA epoxy resin to make advanced epoxy resins having good flame retardant properties along with a higher Tg [22]. He demonstrated that the DEGBA epoxy resin with diphenyl phosphate achieved the highest number of

Table 5.2 Chemical structures of the phosphorous-containing flame retardants and their flame retardancy are presented with % P content and LOI

Phosphorus-containing flame retardants	Curing agents	% P	LOI
 (V)	DDS	9.5	29–31 [20]
 (VI)	DDS	7.8	34 [18]
 (VII)	DDS	1.5	30.5 [19]
 R: Ph (VIII)	DDS	1.1	32 [22]

LOI value and Tg, which was 32 and 190 °C, respectively. A surprised discovery at his study was that the phenomena of intumescing chars formation could be only observed in the cured systems, where the pre-reacted DEGBA with the aryl or alkyl phosphates was cured by DDS curing agent. However, in the same cured DEGBA epoxy resin with DDS, the additive phosphates did not produce good chars formation. The summary of the phosphorus-containing flame retardants and its flammability are presented in Table 5.2.

5.4 Review of Rheological and Mechanical Properties of Advanced Epoxy Resins Containing DOPO-Derivatives

The mobility of an entangled polymer chain is frequently determined by a glass transition temperature, which is an indication of a relaxation statue of the entangled polymer chains. Unlike thermoplastic polymers, epoxy monomers can be

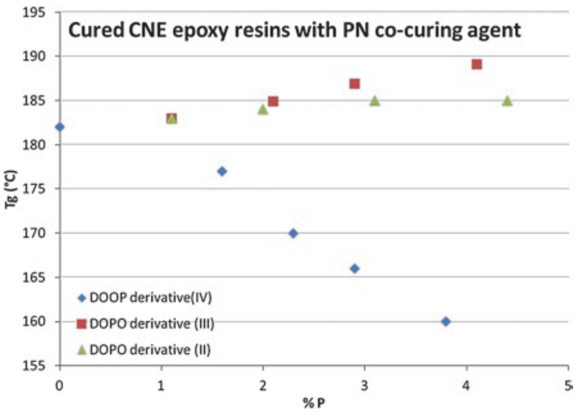


Fig. 5.2 Tg versus % P in cured CNE epoxy resins cured by a mixture of phenolic novolac (PN) with different DOPO derivatives

chemically cross-liked at elevated temperatures by either itself or the aid of curing agents [1]. Thus, a Tg of a cured epoxy resins can depend on the type of epoxy resins, curing agents and curing temperatures as well as flame retardants. It is important for epoxy laminates to obtain higher Tg at a low level of % P content, which may be a key factor to prevent a failure of the PCT (pressure cooker test) or soldering bath at electronic applications [1–4]. As we mentioned at the above section, DOPO derivatives can be used as a co-curing agent. We here have the three DOPO derivatives (II–IV) to present their rheological properties in terms of Tg versus % P content. In Fig. 5.2, from the figure we can see that the two DOPO derivatives (II and III) have increased Tg when % P increases in the cured epoxy resins. Moreover, in case of the DOPO derivative (III), the Tg of the cured epoxy resins are slightly higher than that of the epoxy containing the 1,4-naphthalenediol DOPO (III), which may result from the existence of the resonant structures. However, the Tg of the cured CNE containing the DOPO derivative (IV) decreases as % P increases in the case of the DOPO derivative (IV), which may be explained by a reduced cross-linking density because of the relatively high volume of the bulky DOPO groups [14].

On the other hand, the mechanical strength of cured epoxy resins can be measured by a relationship between storage modules and loss modules at elevated temperatures. Since epoxy laminates are composed of several stacked pregregs it may be a critical point to review what factors can be influenced to the strength. Here is an example of the factors in Figs. 5.3 and 5.4: A relationship between Tg and % P or modulus of pre-reacted DGEBA containing the DOPO derivative (II), which were cured by different curing agents. As we can see from the figures, the higher Tg of the cured epoxy resins is obtained in case of DDS. However, the moduli of DDS-cured epoxy resins are lower than that of PN-cured epoxy resins, which could result from the different reactivity of the two curing agents. Therefore, the evaluation of the rheological and mechanical properties of cured epoxy resins can be considered in explaining how cured epoxy resins are evolved at different curing systems even though it is at the same level of % P content. Eventually, this evaluation would be useful for epoxy laminates applications, where the bonding strength may be a first priority.

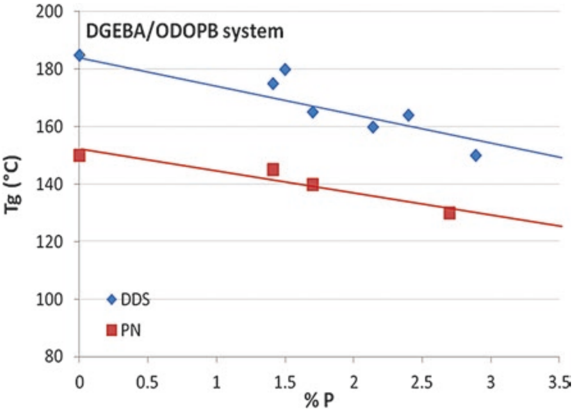


Fig. 5.3 Tg versus % P in cured DGEBA-ODOPB (II) system using different curing agents

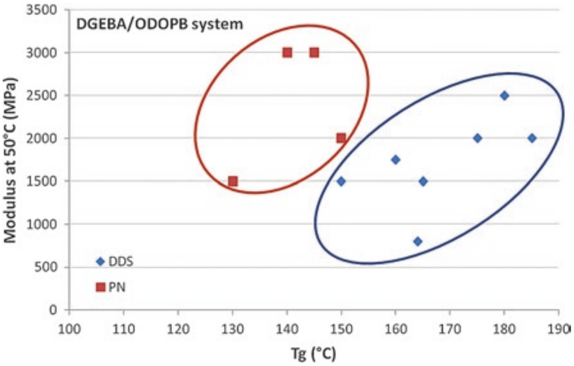


Fig. 5.4 Modulus at 50 °C versus Tg in cured DGEBA-ODOPB (II) system using different curing agents

A relationship between rheological properties of epoxy pregregs and curing processes in laminated structures: The absorption of small oligomers on different geometries surfaces has been extensively studied its thermal and rheological properties since the surface properties are modified by the absorbed substances and the geometries itself. In particular, because of its size nanoparticles are of great interest in academics and industries [7]. Rod-type or hollow-type inorganic particles are relatively in many demands at the field of reinforced composites [1, 2]. Marney et al. showed that phenyl phosphoric acids treated into halloysite nanotubes had a potential for flame retardant and reinforcing fillers in nylon 6 [24]. Lin et al. also demonstrated that the addition of the functionalized halloysites with sodium dodecyl sulfate could improve the thermal stability and mechanical properties of the polystyrene matrix [25]. Nanotubes is also an interesting geometry to be adsorbed with phosphors-containing molecules [26]. Due to the cost-effective aspects, most reinforced polymer composites are filled with rod-type glass or carbon fibers in an industrial scale. On the other hand, epoxy resins are reinforced in forms of pre-greg-mats, where a series of the autoclave-curing processes on epoxy pregregs are involved at elevated temperatures. Thus, the rheological properties of epoxy resins

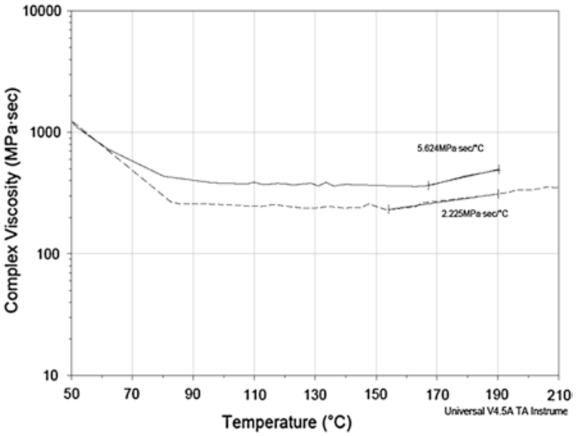


Fig. 5.5 Two traces of the complex viscosity of the B-stage vanished single pregreg containing different epoxy formulations: The *solid line* is representative to CNE/DOPO/PN system and the *dash-line* is representative to CNE/DOPO-BPA/DICY system

on the prepregs-mats is an important property to be used for achieving a good epoxy laminates at the end. Since the epoxy-vanished pregregs are cured with pressure at different temperature profiles the viscosity of the epoxy resins on the pregregs is changed at a different rate with temperature. Thus, obtaining optimized curing process is necessary to impart good physical and chemical properties to epoxy laminates. Dynamic mechanical analysis (DMA) is a typical instrument of measuring the rheological properties of composite materials such as complex viscosity, storage and loss modulus. The complex viscosity of two different single prepreg formulated with different curing agents and DOPO derivatives are presented in Fig. 5.5. As we can see the viscosity graph in the figure, the trace of the complex viscosity from the two single pregregs is relatively same with temperature. However, the temperature at starting to increase the viscosity is different at each epoxy pregreg, where one has a higher temperature and the other has a lower temperature. Moreover, the rate of increasing the viscosity is also different at each case, which may indicate that each epoxy formulation would undergo different curing behaviors.

In the previous paragraph, it has been shown that the viscosity of each single pregreg is changed at a different rate with temperature, which may imply that the rheological properties of epoxy laminates can be changed in a different way. The storage modulus and tan delta of the epoxy laminates, which has the lower rate of the viscosity in the pregregs, are presented in Fig. 5.6. As we can see from the graph, a higher Tg is obtained at the lower curing temperature, whereas a lower Tg is obtained at the higher curing temperature. However, in case of the higher rate of the viscosity in the epoxy pregregs, the trend for Tg is vice versa. In Fig. 5.7, the Tg of the epoxy laminates at 170 °C for 1 h curing time is lower than that of the laminates at 160 °C for the same curing time, which could result from a faster curing process at the high temperature. This difference may be related to the density of cross-linked epoxy resins and the interactions of the polymer chains and the glass-fibers. Thus, it is believed that an optimized temperature and time in the curing process may be significantly dependent upon the viscosity of each pregregs.

Fig. 5.6 The storage modulus and Tg of epoxy laminates formulated with CNE/DOPO-BPA/DICY

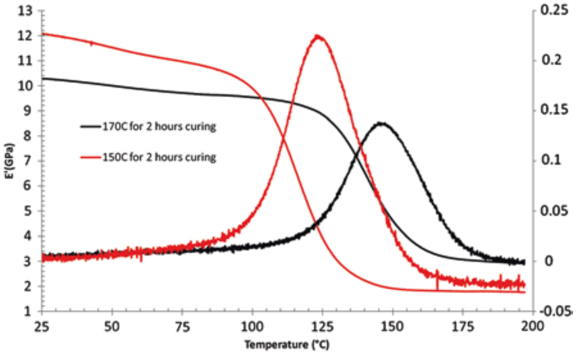
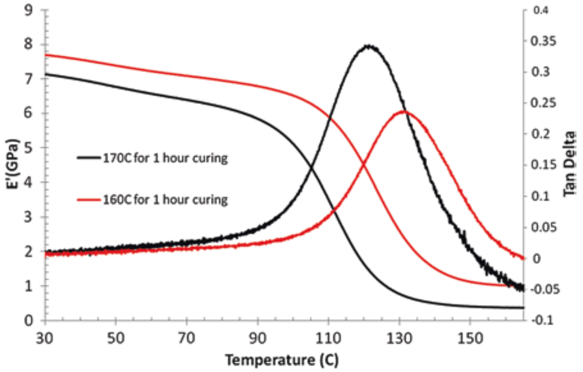


Fig. 5.7 The storage modulus and Tg of epoxy laminates formulated with CNE/DOPO/PN



5.5 Review of Inorganic and Metallic-Based Flame Retardants in Epoxy Resins

Because of the high efficiency of charring process, which results from the reaction of phosphoric acids with decomposed polymers, a series of metal salts of phosphors containing flame retardants were invented and commercialized by Clariant under a trade name of Exolit for thermosetting polymers, where 10–30 parts based 100 part resin was used to obtain the stringent flammability test, such as UL94-V0 and DIN4102 B1 [27, 28]. On the other hand, the use of metal oxides or metal-based compounds recently reveals their potential flammability on polymeric materials due to their versatility to be formed in stable compounds at high temperatures [29–31].

Layered double hydroxides (LDH) with metal ions was first investigated in epoxy resins. Zammarano et al. reported a variety of organic modifiers could be incorporated to magnesium-aluminum(MG) LDH via the ionic exchange method and lead to an increase in d spacing of the MG LDH [30]. They showed that the d spacing of cured DGEBA epoxy resins varied in different organic modifiers, which could result in an occurrence of the self-extinguishing behavior in the UL94 HB test. Manzi-Nshuti et al. [31] investigated three different metal-based flame retardant, CoAl layered-double hydroxide (LDH), Co oxide and zinc acetate dehydrate (ZnAc) on their flammability in a cone calorimetry. They found that a significant reduction on peak heat release rate (PHRR) was obtained by the small amount of zinc acetate dehydrate (ZnAc) added the cured epoxy resins while the addition of either CoAl LDH or colt oxides did not help reducing its PHRR noticeably. Nshuti et al. [31] also demonstrated the flame retardancy of the three zinc-based compounds, where the cured epoxy resin with the zinc hydroxystannate had the two steps of the decomposition while both zinc borate and zinc stannate had one decomposition step as nest cured epoxy resin did. In particular, in the case of zinc hydroxystannate, the highest reduction of pHRR and lowest time to ignition were obtained when its loading was 30 wt% in the cured matrix. Moreover, these zinc-based flame retardants can catalyze the promotion of chars formation when they are combined with melamine phosphates or aluminum phosphinates and borates [32].

Another approach for flame retarding epoxy resins is the use of nanoparticles. It already has been proved that an inclusion of nanoparticles can impart superior thermal and mechanical properties such as an improvement of heat distortion temperature and a significant improvement of modules and strength [33–37]. However, there is one of important technical concerns using nanoparticles: How nanoparticle are dispersed in a polymer matrix [35]. Recently, Pack et al. demonstrated a combination of two nanoparticles with different surface energy and interaction at the interfaces could help improve their dispersion in the polymer blends [36] later they showed that a direct absorption of the phosphors-based flame retardant was successfully achieved onto the montmorillonite (MMT) clays, which could be really exfoliated in several thermoplastic polymers and improve the compatibility of the polymer blends [37].

In contrast to thermoplastic polymers, the structure of a cross-linked network is various in each of thermosetting polymers system. Although the curing process of an epoxy resin is governed by the type of epoxy groups and curing agents, it becomes more dependent upon a degree of the nanoparticles in cured epoxy resins. A comprehensive review paper for CNT-epoxy composites reported that the physical and chemical aspects of CNT to epoxy monomers and curing agents could alter its curing reactions [38]. Since the use of CNT had some disadvantages in polymers and polymer compounds, such as its color and the possibility of toxic gases released when it is burnt, more environmental friendly nanotubes has been in great demand, which could lead to the research developments of Halloysite nanotubes (HNTs). Several research groups already reported their possibility in nanocomposites [39–41]. Deng et al. [41] showed that the different chemical treatments affected on HNTs dispersion in the cured epoxy matrix, where a combination of a phosphoric acid treated HNTs with the enhanced ball mill process could improve the degree of dispersion of HNTs in the matrix.

5.6 Conclusion

We first reviewed the flame retardancy of DOPO derivatives and DOPO-free derivatives in cured epoxy resins. Most works had focus on their possibility of being used as co-curing agent, which could result in reducing the amount of % P for obtaining good flame retardancy, such as UL94-V0 and above 30 in LOI, significantly. Moreover, better materials properties of cured epoxy resins could be achieved when they were pre-reacted with epoxy resins. We also investigated that the rheological/mechanical properties of cured epoxy resins was adjustable by the curing agents and the flame retardants, which would predict the physical properties of epoxy laminates. In the review of flame retardancy of the inorgano-metalic compounds, they were relatively easier to be applied in epoxy resins but still have not been enough studied for their flame retardancy in epoxy resins matrix. Finally, the possibility of using nanoparticles in epoxy-based nanocomposites was briefly reviewed. The improvement of the nanoparticles dispersion could be one of key elements to be overcome during the curing process.

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Chapter 6
Flame Retardant/Resistant Based Nanocomposites in Textile

F. Rault, S. Giraud and F. Salaün

Abstract Due to the increasing consideration in nanotechnology during the past decade, numerous studies were undertaken in improving the flame retardancy properties of natural, artificial and synthetic fibers as well as fabrics by applying nanocomposite approach. This chapter considers key issues concerning traditional and novel approaches or processes to develop nanocomposites coating, nanocoatings on textile as well as the incorporation of nanoparticles into fibers. The incorporation of nanocomposite to form flame retardant coatings onto the surface of textiles or to functionalize fibers by melt spinning which can be subsequently woven or knitted are mainly related for application fields required high performance such as automotive, protective clothing, etc.

6.1 Introduction

Textiles and wider fibrous materials are materials that exhibit depending on technologies (weaving, knitting, nonwovens, breading) extremely varied forms and are used as such or combined with other materials for a variety of applications that are limited not only to the basic function of dressing. Fibrous materials are present all around us: they are multifunctional materials with textile protection against all kinds of

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aggression; textile coverings may be flame retardant (FR), cutting and stab resistant, and bullet proof. There are smart textiles integrating sensors or becoming themselves sensors with electro conductive fabrics, there are also cosmetic textile with refreshing textile or slimming textiles. Fibrous materials are the base of composite materials; they are the reinforced composite materials present in the automotive, aerospace, and all other composite applications. Textile are also fishing nets, geotextiles, stretched structures or insulating material for buildings, any kind of filter based on nonwovens, textile is used in medical applications like human implants such as artificial arteries. Apart protective clothing, heat and fire resistant textiles are needed in areas where fire protection is essential namely transport and housing with furniture, bedding, seat cover, interior (floor and wall covering), structural composite materials, filters, insulation acoustic and thermal panels …. The key element of textile is fiber. At the beginning natural and then artificial, from the second half of the 20th century with the development of polymers, are now synthetic fibers which have world's largest production. More recently, synthetic fibers called high performance are widely used for technical textiles. There are many heat-stable fibers (polyaramids, fluorocarbon, melamine, polybenzimidazoles, polyimides, polyoxazoles, polyphenylene sulfides …) that are inherently fire resistant. However, for various reasons (economic, ease of implementation, conservation of secondary functionality …), the fire behavior improvement of common fibers remains a major challenge. The nanomaterials strategy is one of several principles for improving the burning behavior of textiles.

The development of nanostructured structure textile to improve performances and/or new functions has gained considerable attention for several years, especially to textile applications polymer matrix. The main benefit is the increasing of the strength of the materials by adding of exfoliated clays, nanoparticles and carbon nanotubes. Nevertheless the application of nanotechnology in textile field allows producing multifunctional substrates such as antibacterial, superhydrophobic and also fire retardant. In order to obtain materials with the desired performance, two principle ways can be considered to bring the properties, e.g. melt spinning and fiber surface finishing treatments.

Before detailing the various principles of nanostructured textiles and their fire behavior, it is necessary firstly to recall the classic flame retardants for plastics and textiles and secondly to present the specifics of the fire behavior of textile material. Textile including nanomaterials can be divided into two main groups, in which the nanostructured materials refer to condensed bulk materials and nanophase/nanoparticle materials are usually dispersive nanoparticles [1]. Nanomaterials usually used in textile field such as textile structures, finishes and coating are mainly nanofibers, polymer nanocomposites, and/or nanostructured surfaces. Textile requires effective flame retardancy properties with a minimal environmental impact, since these structures are often washed and flame retardant additives of coating can leach out into the environment [2, 3].

6.2 Flame Retardant for Plastic

The chemical nature of flame-retardant additives for plastic is highly varied and the action of these compounds is not only optimized for a particular polymer chemistry but also to prevent flammability effects such as flame spread, smoke release, dripping… Thus, the choice of the additives should take in account the chemical nature of the plastic and the end-use application.

World-wide 1.8 billion kilo of fire retardant additives are used annually [4]:

- 700 million kilo of halogenated fire retardants;
- 200 million kilo of organophosphorous fire retardants;
- 750 million kilo of aluminium hydroxide fire retardants;
- 150 million kilo of other fire retardants.

Halogenated fire retardants are still used on a very large scale, mainly because they have the least effect on the mechanical properties of the materials and are cost-effective. In many cases replacements of halogenated flame retardants have already been found. Some progresses were especially made in the field of phosphorous-nitrogen and metal hydroxide compounds. New compounds are developed and synergistic formulations are found that boost the performance. However, the mechanical properties of materials after FR addition ares till worse than the ones using halogenated flame retardants.

6.2.1 Mode of Actions

Flame retardant additives may have a mode of action in gas phase to extinguish the flame by radical inhibition or dilution, that leading to the decrease of the flame temperature or to reduce the availability of flammable gases and oxygen; and/or in condensed phase, in the vicinity of the flame to perturb the thermal degradation of the substrate by dehydration and char formation. Therefore, according to the chemical nature and the stage of the combustion process acting, the action modes can be classified into five categories, i.e. gas dilution involving the use of additives which decompose into non-flammable gases and lead to reduction of both fuel and oxygen levels; thermal quenching in which flame retardants reduce the rate of burning by endothermic decomposition; protective coating when the additives induce the formation of a barrier or a thermal shield; physical dilution with the incorporation of an inert and non-flammable component; and chemical interaction, when the flame retardant additive decomposes into radical species in competition with the burning process. The flame retardant compounds can be classified either according to their chemical structure or their mode of action to provide fire resistance. Flame-retardant materials are a major business for the chemical industry and can be found practically everywhere in modern society. However, many additives have detrimental effects on the environment and human health and thus should be limited in use.

6.2.2 Halogen-Containing Flame Retardants

The halogen-containing flame retardants, used in most of cases in combination with metal compounds, show a chemical action in gas phase, even if the condensed phase reactions with the polymer could be involved. These compounds are based on chlorine and bromine to react with flammable gases to significantly reduce the combustion rate by radical transfer. Thus, during the first step of the reaction, the halogen compounds interrupt the chain reaction of combustion by the release of halogen hydracids which transform the highly reactive radicals, $OH^{\bullet}$ and $H^{\bullet}$ by less reactive radicals. Thus, the effectiveness of halogen compounds depends mainly on the ease of release the halogen and on the nature of the group containing the halogen. To achieve good levels of flame retardancy, high concentrations, 40 wt% for chloride and 20 wt% for bromide, are required [5]. Therefore to reduce the halogen concentration and to enhance significantly flame retardant properties, several metal compounds such as metal oxide, could be used as synergists. Amongst these synergistic agents, antimony trioxide plays the role of an inhibitor in the gas phase, others common synergists are phosphorus, nitrogen, zinc and tin-containing compounds. Nevertheless, these compounds are less and less used since they release during their degradation toxic gases and corrosives as dioxins, benzofurans, HCl and HBr and they also present some environmental health hazards. Thus, some compounds such as brominated flame retardants have in effect been banned via the RoHS directive (2002/95/EC), but this does not imply that all other flame retardants are free from health and environmental concerns.

6.2.3 Inorganic Compounds

Amongst the four mains families of flame retardant chemicals, metal hydroxide compounds offer an attractive alternative to halogenated formulations lying in their low toxicity, corrosion properties and emission of smoke during processing and burning. Thus, these compounds decompose endothermically and release water, which reduce the heat and temperature from the substrate. Typical metal hydroxide flame retardants are aluminium trihydroxide, magnesium carbonate, magnesium hydroxide, zinc borate and calcium borate. Furthermore, as cited by Chen and Wang [6], $Al(OH)_3$ and $Mg(OH)_2$ are the most important metal hydroxides used as flame retardants in polymer materials and the effects of these compounds were found similar in the improvement of flame-retardant properties, even if $Al(OH)_3$ was superior by the cone calorimetric test. Besides, the nano-scale $Mg(OH)_2$ have better flame retardancy than micro-sized.

Inorganic compounds, as hydrates of aluminium and magnesium based on endothermic additives are used to slow down the rate of pyrolysis. They have rather low prices, low toxicities but high loading content is required to provide the fire performances of interest [7–10], and therefore it results in the decrease of the mechanical properties of the polymer. This class of compounds acts simultaneously in gas and condensed phase, when their endothermic decomposition induces in one part the water release to cool down the system and to dilute fuels in the flame zone and in other part the forming a metal oxide barrier. Aluminium and magnesium hydroxide, which decompose thermally in the temperature range of 180–240 and 330–360 °C, respectively [11], are widely used as halogen free alternative to brominated flame retardants, as well as inorganic phosphorus. This inorganic group, containing also boron salts, inorganic antimony, tin, zinc and red phosphorus, represent around 50 % by volume of the global flame retardant production.

6.2.4 Charring and Intumescent Systems

Among the flame retardants for polymers, intumescent flame retardant (IFR) has been very carefully studied in recent years, since they represent an environmental friendly alternative to the traditional halogen-containing compounds. Even if intumescent systems have existed since the 1940s in paint industry, they have only appeared in the textile field market for about 30 years. Furthermore, IFR presents many advantages compared to halogen-containing flame retardants, such as less toxicity, less acidic fumes during the burning process [12]. Flame retarding textile substrate by intumescence process has been known for several years and is essentially a special case of a condensed phase mechanism [13–19]. Intumescent systems interrupt the self-sustained combustion of the polymer at the thermal degradation with evolution of gaseous fuels. And thus, the intumescence process results from a combination of charring and foaming of the surface, limiting heat and mass transfer between the gas and the condensed phases and the flame and the substrate [15]. Furthermore, the layer inhibits the evolution of volatile fuels via an entrapment process, which limits the oxygen diffusion to the polymer bulk [13]. Intumescent formulations contain three kind of active additives [20, 21], i.e. an acid source or precursor for catalytic acidic species which can be an acid (phosphoric, sulphuric, boric), ammonium salts (phosphates or polyphosphate, sulfates, halides), a phosphate of amine or amide (urea, melamine phosphate, …) or an organophosphorus compound as tricresyl phosphate, alkyl phosphate or haloalkyl phosphate; a carbonic or polyhydric source such as starch, dextrin, sorbitol, pentaerythritol or methylol melamine; and a blowing or spumific agent like urea, urea-formaldehyde resin, dicyandiamide, melamine or polyamide. The carbonic source additive is not necessary when the treated material has an intrinsic charring behavior as for example most of polyamides, polyurethanes and carbohydrate polymers (cellulose). Contrary to these polymers having intrinsic charring behavior, the presence of charring agent in IFR system is required for polyolefin as PP which is the most studied. The most widely reported IFR for replacing halogen-containing agent is phosphorus-nitrogen containing compounds. Thus, the IFR formulations for PP include generally these kinds of system, i.e. ammonium polyphosphate—melamine-pentaerythritol [22]; ammonium polyphosphate—triazine compound, mixture of melamine phosphate with pentaerythritol [23] or their reaction products and these derivative compounds [24, 25] in addition with a charring polymer [26, 27]. However, these conventional intumescent flame retardant agents need to be improved and especially by the addition of synergistic agent such as zeolithe [28–30], montmorillonite [31, 32] or sepiolite [29], silicotungstic acid [33], metal oxide [34–37], silica or alumina [38], or in working condition to adjust the relative ratio of each component [39]. Furthermore, the high loading content of IFR additive leads to a decrease in the mechanical properties of the polymer, and most of the time these compounds being highly polar induce the problem of water leaching. Several authors reported the possibility to decrease the polarity and therefore to improve the compatibility with polypropylene by using reactive extrusion to synthesize melamine salt of pentaerythritol phosphate [40, 41].

Unfortunately, conventional IFR systems have presented some drawbacks. Acid sources and charring agents are globally hydrophilic chemicals. They have some problems such as moisture sensitivity and poor compatibility in polymer matrix in particularly in non-polar polymer like PP. Migration phenomenon could occur during the processing, the application or the ageing of the material. Thus, exudation and high water solubility are encountered problems, which lead to the loss of FR properties [15]. Moreover conventional IFR systems show efficiency only from 20 wt% loading. The minimum loading of IFR systems and the poor compatibility of their components induce homogeneity problems; create damage of the surface quality and decrease of mechanical properties for the final material. Finally, the necessity to have the three components of IFR system is not convenient for the industrial implement of final PP materials. These drawbacks make impossible the introduction of conventional IFR systems in the core of PP fiber by melt spinning process. Indeed, it is well-known that moreover the high level of fillers is incompatible and induces some problems during the drawing step. Thereby, the coating process still needs a possible way to apply IFR formulation on PP fabrics. However the loss of handle is one of disadvantage of this process without to solve problems of IFR systems.

The concept of microencapsulation is a way to solve the different drawbacks of conventional IFR systems. Microencapsulation is a process of enveloping microscopic amounts of matter (solid particles, droplets of liquids or gas bubbles) in a thin film of polymer which forms a solid wall (microcapsule) or inside a polymeric matrix (microsphere). These structures allow the isolation of the encapsulated substance from the immediate surroundings and thus protect it from any degrading factors such as water. Also the microencapsulation processes allow encapsulating acid source of IFR system and protects it from any degrading factors such as moisture. The polymeric membrane of microcapsule permits also to improve the compatibility of acid source in the materials and thus to keep FR and mechanical properties. Moreover, the polymeric matrix or membrane of microcapsules should be appropriately chosen in order to have the chemical characteristics of charring agent and/or blowing agent (polyurethane, aminoplast resin, isocyanurate). Also, the combination of the encapsulated acid source and the microcapsule membrane with charring and/or blowing properties form an intrinsic IFR formulation. The concept to have “all in one system” makes easier the IFR incorporation system into polymeric matrix.

6.2.5 Nanocomposites

A material is considered as nanocomposite if nanofillers in the polymer matrix are uniformly dispersed in preserving its nanometric size (without agglomerate). Obtaining a real nanocomposite is not so easy despite the improvements of effective implementation technologies. The desired properties of the material are obtained only if the polymer matrix contains uniformly fillers remained nanoscale [42–52]. The properties of nanocomposite material are governed mainly by the dominance of the interfacial structure. Thus thermal and fire decomposition mechanisms of the nanocomposite are totally different from those of the polymer matrix alone. Under the stress of a fire, the presence of nanofillers generally used to delay the depolymerisation of the polymer and thus reduce the amount of released heat [48, 49]. Nanofillers most studied to improve the fire behavior of almost all conventional polymers are clays (natural or synthetic), carbon nanotubes and nanofibers. In the case of clay, it appears that the viscosity of the molten polymer is larger and the pyrolysis of the polymer is hindered by the formation of a clay-rich layer which acts as a barrier to fuel [53, 54]. With carbon nanotubes or nanofibers, there is the formation of a network of nanoparticles which also allows the molten polymer to viscosity and reduce the gas release [55, 56]. The nanofiller may be associated with conventional flame retardants to obtain a synergistic effect for decreasing the amount of these latter in the polymer matrix while achieving the required levels of certain standards [48, 49].

6.3 Flame Retardancy of Textile

The fire behavior of a fabric largely depends on the chemical nature of the fibers that compose it. Also the same major flame retardant products for polymeric materials in general are found in textiles. However, textile materials have several characteristics. Regarding their fire behavior, textiles generally exhibit large specific surface and ease of access to atmospheric oxygen which causes a faster ignition compared to a full plastic material. Their physical characteristics (surface area and linear aspect of fiber/yarn) and their specifications (washability), application techniques of fire retardant products for textile materials are very diverse and differ from plastic materials. This part shows the outline of the burning behavior of textiles [57, 58] and their products fire retardant [2, 3, 57] that have already the subject of many reviews.

6.3.1 Burning Behavior and Fire Hazard of Textile

The burning behavior of fibers is influenced by thermal transition temperatures and thermodynamics parameters. Table 6.1 lists the commonly available fibers with their ignition temperature and the behavior when approaching a flame.

It is recognized that fiber is flammable if its ignition temperature is low and its flame is hot. This is particularly true for cellulose fibers and some synthetic fibers like acrylic. LOI (Limiting Oxygen Index) of common fibers is also given in the Table 6.1. LOI is the minimum concentration of oxygen in order to insure the combustion of the matter. Knowing that the concentration of oxygen in air is 20.8 %, the fibers with a LOI less than or equal to 21 % ignite easily and burn quickly. From 26 %, the fibers have typically flame retardant behavior and textiles from these fibers pass most of the fire tests. It should be noted that the cellulose fibers, wool and nylon are naturally charring contrary to polypropylene and polyester. This difference in thermal degradation was key strategies to improve the fire performance of these fibers. For the former, fire retardant products have the primary role to emphasize the char formation to reduce the release of fuel. For the latter, the flame inhibitor products (action in phase) were selected: their action is coordinated to the fact that these fibers by melting flee the fire that does not spread to the rest textile. Textiles without fire retardant treatment have several specific risks with respect to the fire, especially if the fabric is in direct contact with humans (clothing, furniture). As indicated in Table 6.1, of these dangers, we

Table 6.1 Ignition temperature, limiting oxygen index and flammability of commonly used fibers [57, 58]

Fiber	Ignit. temp. (°C)	LOI (%)	Flammability
Wool	600	25	Supports combustion with difficulty
Cotton	350	18.4	Burns readily with char formation and afterglow
Viscose	420	18.9	Burns readily with char formation and afterglow
Nylon 6	450	20–21.5	Melts, supports combustion with difficulty
Nylon 6.6	530	20–21.5	Melts, does not readily support combustion
Polyester	480	20–21	Burns readily with melting and soot
Acrylic	>250	18.2	Burns readily with melting and sputtering
Polypropylene	550	18.6	Burns slowly
Modacrylic	690	29–30	Melts, burns very slowly
Polyvinyl chloride	450	37–39	Does not support combustion
p-aramid (e.g. Kevlar)	>550	29	Self-extinguishing
Polybenzimidazole (PBI)	>450	40–42	Incombustible

Table 6.2 Smoke emission from fabrics made from different fibers or blends [57]

Sample	Decrease in visibility (%)	Optical density
Acrylic	97	1.5
Cotton	4	0.02
Cotton, flame-resist treated	98	1.7
Rayon	4	0.02
Wool	18	0.09
Nylon	6	0.03
Polyester	28	0.14
65 % polyester—35 % cotton	99	2.00
55 % polyester—45 % wool	98	1.70
Polyvinyl chloride	34	0.18

should note the risk of falling melt matter inflamed or not causing direct burns and also the spread of fire. This is the case of textiles base only conventional flammable synthetic fibers.

Like all types of materials, the burning behavior of textiles depends on many external factors (nature, duration and placement of ignition, material orientation, ventilation …). Apart from the nature of the fibers used, some physical characteristics of the textile also play a role in fire behavior. Thus, a fabric with a low surface density (open structure) increases the burning rate [59]. Other parameters as effect of yarn geometry and fabric structure have an influence less obvious on flame behavior.

The leading cause of death in a fire is smoke on the one hand by its opacity generating panic and disorientation and secondly by its toxicity [60]. Table 6.2 provides an indication of the amount of smoke released by fabrics made of different fibers or blends. Aliphatic polymers are those which release less smoke the same when they have heteroatoms (cotton, nylon, wool). Furthermore, the quantities of smoke released by fabrics from fiber blends are very difficult to predict. Indeed both polyester/wool and polyester/cotton blends release a much greater amount of smoke than the fibers alone. Finally, the presence of fire retardant in a material usually leads to a larger amount of smoke either by inhibition of the oxidation reaction generating incomplete combustion (fire retardant agent acting in the gas phase such as those based on halogen) or by reduction of the heat flux that the flaming combustion turns at time into smoldering.

6.3.2 Flammability Testing of Textiles

The fire standards for textiles are extremely numerous, not only because each country has its own regulation, but also because the textile fire standards are moreover available by sectors and end-use applications (curtains, nightwear, protective clothing, furnishing, bedding, aircraft seats, railway seat…). Most common textile flammability tests are currently based on ease of ignition and/or burning rate behavior which permit to compare easily fabrics and composites in varying geometries. These fire tests use as a source of ignition "small" flame, and among these the most emblematic tests is the vertical test or equivalent (ISO 6940). Specific tests to the final application (bedding, furniture) refer to sources of ignition (match and cigarette) present in the actual conditions of use of textiles. However, it is widely accepted that in actual fire conditions, the most critical feature in propensity to fire spread is the heat released rate of the material. Only textiles used in building materials, aircraft and transport interiors and seating are required to have minimal levels of heat release rate (HRR, peak of heat release rate PHRR), which is measured mainly by cone calorimeter [61].

6.3.3 Flame Retarding Systems for Textile

Flame retarding systems for textiles are divided into three main groups: (i) Nonreactive systems; (ii) Reactive system; (iii) Inherently FR fiber. For the first two groups, the FR system is applied to the textile substrate (woven, knitted, nonwoven). Currently available commercial FR reactive and nonreactive treatments are listed in Table 6.3. In the case of nonreactive systems, there is no chemical reaction between the FR agent and the fiber. Several processes are within this category. With conventional finishes by padding, by spraying or by exhaustion from bath, the FR agent is deposited on the surface of fabrics (cohesion by Van der Waals forces). The durability of the treatment is often improved either with insolubilisation of FR agent or with the addition of a binder (resin). There is also for specific applications (furniture, transport, technical textiles), the deposition of a coating or back-coating (mainly acrylics, silicone or polyurethane) containing FR agent on the fabric. In reactive systems, the processes need advanced requirements (e.g. ammonia gas cure unit). The FR treatment is obtained with chemical reactions from FR agent; either FR agent and fiber react together with covalent link (graft copolymerization of FR with fiber) or there is in situ polymerization of FR compounds on the surface of the fiber. The reactive treatments are intended to be durable, i.e. that the fire retardant properties are retained beyond 50 washes. In the third group, we find man-made inherently FR fibers which may be derived from various techniques. The FR agent could be directly incorporating in fiber during spinning process. Otherwise the fiber could be produced by copolymerization of FR compounds with fiber-forming monomers. The last case concerns advanced spinning processes with thermostable aromatic polymers (Polyarmids, e.g.: Nomex, Kevlar, Twaron; Poly(aramid-arimid), e.g.: Kermel; Novoloid, e.g.: Kynol; Polybenzimidazole, e.g.: PBI; Carbonized acrylics, e.g.: Panox). The Table 6.4 gives the currently inherently FR man-made fibers (except thermostable aromatic fibers).

Table 6.3 Principal examples of currently available FR treatments for textiles [3]

Substrate textile fiber(s)	Generic formula	Comments
Cellulose (cotton, viscose and cotton-rich blends)		
Non-durable	Ammonium phosphates and mixtures with other salts; ammonium polyphosphate; organic N- and P-containing compounds; bore derivatives (Borax)	Available as proprietary formulations; semi-durability may be developed by post-curing to achieve cellulose phosphorylation or by addition of resins
Durable	Tetrakis (hydroxymethyl) phosphonium salt (THPX) adduct condensates N-methylol and N,N′-dimethyloldialkylp hosphonopropionamides and derivatives	Typified by the ammonia-cured Proban® (Solvay) Exemplified by Pyrovatex® (Huntsman) its variations and equivalents. Requires presence of cross-linking resins
Back-coatings (application to most textile substrates)	Halogen-organic antimony III oxide (ATO) formulations Intumescent-based systems	Durability is determined by resin choice
Wool durable to dry cleaning	Zirconium and titanium hexafluoride complexes Tetrabromophthalic anhydride (TBPA)	Typified by Zirpro®
Polyester: durable	Cyclic organophosphonate	Amgard CT (Rhodia) applied by thermofixation
Polyamide: durable	N- and S-containing polycondensates typically based on thiourea-formaldehyde formulations	Find application in technical fabrics
Acrylics and multifiber blends and composites (e.g. furnishing fabrics)	Back-coatings based on halogen-ATO formulations	The only commercial alternatives to using modacrylic fibers, e.g. Kanecaron

Table 6.4 Inherently FR man-made fibers currently in use [3]

Fiber	Additive or comonomer	Comments
Viscose rayon	Cyclodithiophosphoric-anhydre additive	Developed in the 1970s now available as Exolit 5060 PK (Clariant) Lenzing FR®
Modacrylic	15–65 % vinylidene (or vinyl) chloride	Developed in the 1950s and still produced in Japan (Kanecaron)
Polyester	Difunctionalphosphinic acid or ester	Developed in the 1970s as Trevira CS®: the most established inherently FR polyester
Polypropylene	Halogen—organic synergist (ATO or tin derivatives) formulations	Recent developments of hindered amine chemistry enable single halogen-organics to be used

The currently FR treatments and fibers come from the chemistry between 1950 and 1980. The commercial development is completely linked to changes in legislation and regulations. The evolution of these treatments and fibers has been guided by the desire to achieve better performance (fire resistance, durability) for an ever lower cost. However it is the environmental and toxicological aspects past 20 years have been responsible for banning certain products (brominated) or certain processes (release of formaldehyde or acrylamide). Thus research continues to find improvements and alternatives.

For cellulosics, the durable reactive systems with real advantages (durability even for high temperature wash cycles as in hospital) keep significant drawbacks namely on the one hand for Proban® (and derivatives) special requirement (ammonia gas cure unit) and loss in softness for the fabrics, and on the other hand for Pyrovatex® (and derivatives) losses in tensile/tear strengths and formaldehyde release during application and end-use. Despite several recent attempts [62–67], development of a reactive FR species remains a challenge where the covalent bonds with cellulose are done with easy textile processing and are resistant to hydrolysis.

Even if halogen—organic antimony III oxide still the usual formulation for back-coating, environmental concerns encourage to phosphorus-nitrogen containing species (including intumescence formulation). However, formulations with the latter need to be improved to reach in one hand the same efficiency (e.g. by obtaining FR vapor-phase activity [68]) and in other hand the same durability (reduction solubility [69]).

Several sectors including railways need more and more barrier fire resistant fabrics even when they are composed of melt fusible fibers as polyester or polypropylene. To meet this need without necessarily recourse to back-coating, attempts to develop char-promoting retardants for these fibers has been made [70–73].

Among alternatives in order to pass these different challenges, nanotechnology offers opportunities which are developed following.

6.4 Strategies with Nanocomposite Principle and Their Fire Properties for Textiles

Textile functionalization by material modification can be obtained following three main ways, i.e. (i) incorporation of functional additives into the polymer melt or polymer solution before spinning; (ii) chemical grafting of additives on the fiber surface with or without using linkers; and (iii) formation of a coating onto the surface of fiber or fabric. Each process has some advantages and drawbacks and the choice depends not only on the chemical nature of the substrate but also on the permanence of the treatment and the end use of the textile. Thus, spinning offers high permanence but is not practicable to natural fiber, chemical grafting requires the presence of reactive or functional chemical groups onto the surface of the substrate; and coating, the most universal method, is independent from textile type, low amount of additives can be used and this technique allows the combination of different functionalities [74].

6.4.1 Spinning Processes

6.4.1.1 Polyolefins

As the polyamide, the polypropylene (PP) is one of the most widely used polymers in the textile field. Indeed, this polyolefin exhibits an attractive combination of low cost, low weight, easy processing, and extraordinary versatility in terms of properties (it is known for its balance of strength, modulus and chemical resistance). However, PP presents a high flammability because of its wholly aliphatic hydrocarbon structures. In the last decades, many studies were carried out to improve its flame retardancy by adding different species of nanofillers into the polymer before the spinning process.

The most frequently used nanoparticle, i.e.: layered silicates, was also investigated to enhance the flame retardancy properties of polypropylene textile articles. For example, Horrocks and co-workers evaluated by cone calorimetry the flammability of PP fabrics containing different concentrations of maleic-anhydride grafted PP and montmorillonite clay modified with dimethyl, dihydrogenated tallow quaternary ammonium Chloride (Cloisite® 20A, Southern Clay Products) [75]. Although an evident char formation in samples containing clay was seen, no clear flame retardancy properties were conferred to the PP samples. This research team continued these works by studying the impact of four different functionalized clays (tree montmorillonite clays supplied by Southern Clay Products: Cloisite® 20A, Cloisite® 30B, a montmorillonite later modified with vinyltriphenylphosphonum bromide and a bentonite clay from Elementis: Bentone 107) in the presence or absence of two types of grafted PP as well as with or without conventional phosphorous flame retardant: ammonium polyphosphate (APP, Albemarle Corporation) [76]. Due to the difficulty to obtain accurate reproducible results from thin fabrics with cone calorimeter, they performed a small scale spread test based on British Standard BS 5438. These experiments demonstrated again a change of the burning behavior in presence of clay. Whatever the clay introduced into the PP with or without compatibilizing agent, a trend of self-extinction was noticed. However, in the presence of APP, burning behavior became more erratic with no significant improvement, which reveals the absence of synergy between this fire retardant additive and clays. Apart the combination of nanofillers with conventional flame retardants, others potential synergistic associations can be imagined. Thus, based on the works of Peeterbroeck et al. [77], who showed a superior decrease of HRR for ethylene vinyl acetate containing simultaneously carbon nanotubes and clay, we studied as potential synergy the use of clay with another carbonaceous filler, i.e.: graphite [78]. Polypropylene composites reinforced with Cloisite® 15A and/or graphite were prepared by melt blending from which multifilament yarns and knitted fabrics were produced. Despite a slight synergistic thermal effect between clay and graphite was shown from the curves of weight difference extracted from TGA experiments, no reduction in PHRR values occurred for samples containing the both fillers during mass loss calorimeter test under a heat flux of 35 kW/m^2.

About the use of synthetic clay i.e. polysilsesquioxanes (POSS) in PP, the latter appears not sufficient to obtain performance required in several fields of application, even if, the authors have observed some improvements in fire behavior [79]. Bourbigot et al. showed that the time to ignition of PP knitted fabric filled with FQ-POSS nanoparticles (poly(vinylsilesquioxane), Hybrid Plastics) was delayed about 50 s compared to that of virgin PP [80]. However, apart a translation of the HRR curve recorded during cone calorimeter experiment under a heat flux of 35 kW/m^2, no significant modification in terms of PHRR or total heat release (THR) was noticed which reveals this nanofiller act more as heat stabilizer than as flame retardant.

It is well recognized that filler geometry may play an important role on the final properties of nanocomposites fibers. Thus, in our laboratory, we were interested to fillers having fiber-like shape (carbon nanotube, sepiolite) rather than layered form such as montmorillonite, bentonite, graphite, etc. Thus, it was highlighted that the introduction of 1 wt% of multiwalled carbon nanotubes allows to increase the thermal stability and to decrease of 50 % the HRR peak of PP knitted fabrics if examined by cone calorimeter with a heat flux at 35 kW/m^2 [81]. However, the time to ignition decreased from 59 to 38 s for PP fabrics containing carbon nanotubes. Two reasons were proposed to explain this behavior. The first explanation was attributed to a fibrillation of the nanocomposite multifilament during the process of knitting. Indeed, the fibrils that appear at the surface of the samples can facilitate the ignition. The second one can be due to an increase in the radiation in-depth absorption coefficient induced by the addition of fillers. We again demonstrated a similar reduction of the time to ignition with polypropylene knitted fabrics filled with 0.75 wt% of modified and non-modified carbon nanotubes, without providing nevertheless a decrease of HRR [82]. In the same study, mass loss calorimeter measurements were made on PP knitted fabrics containing 0.75 wt% of functionalized sepiolite exposed to an external heat flux of 35 kW/m^2. Nanocomposite fabrics exhibited a decrease of about 20 % of PHRR compared with unfilled PP. Therefore, we explained this reduction by the formation of char when knitted fabrics are burnt. However, we assumed that the char was not enough to insulate the material because the THR recorded for samples with or without sepiolite was comparable.

Apart from clays such as montmorillonite, bentonite, sepiolite and carbonaceous fillers such as graphite or carbon nanotubes, other nanoparticles were introduced into PP fibers to improve their fire properties. Thus, we investigated the fire behavior modification of PP knitted fabrics containing manganese oxides (MnO or Mn_2O_3) or manganese oxalate (MnC_2O_4) [83], while Dogan and co-workers studied by MCC the flame retardant properties of PP fibers filled with BPO_4 [84]. Despite the promising results achieved by these researchers for PA6 fibers containing BPO_4, no decrease of the PHRR or THR was seen this time for PP. The same results were obtained for PP fabrics filled with based manganese nanoparticles. In the both cases, this behavior is attributed to the absence of char formation. The aforementioned nanoparticles are not able to form a continuous shield able to protect the polymer which explains why no reduction is observed for these PP composites. The flame retardancy behavior of polypropylene/nano-SiO_2 composite textile filament was also investigated by Erdem et al. [85]. In this later study, the combustibility of fibers samples containing 0.3, 1 or 3 wt% of SiO_2 spherical nanoparticles were determined by Limit Oxygen Index (LOI) test. The authors showed that the LOI of the neat filament was about 18 % and the LOI of PP composite filaments didn't exceed 18 %, whatever the content of SiO_2 nanoparticles. From these experiments, it can be concluded that none of the sample reached the requirement of fire-retardant filament.

The development of fire retardant polyolefin nanocomposite fiber was undoubtedly focused on the polypropylene. However, little is known about the effects of nanoparticles on the fire properties of polyethylene fibers. Zhang et al. undertook the preparation of ultrahigh molecular weight polyethylene (UHMWPE) nanocomposite fibers by a gel-spinning process [86]. First of all, they incorporated magnesium hydroxide ($Mg(OH)_2$) nanoparticles into the polymer by dissolving UHMWPE powder in an homogeneous suspension of nanoparticle and solvent (Decalin: decahydronaphthalene, trans + cis, 98 %). Then, the polymer solutions were extruded with the help of pressurized nitrogen through an orifice of a spinneret. Finally, the filament was quenched into ice water batch to form precursor gel fiber which was subsequently hot-drawn. In order to have a better understanding of the flame retardant mechanism of $Mg(OH)_2$ nanoparticles for the UHMWPE nanocomposite fiber, the authors proposed to monitor the flaming process from thermogravimetric (TGA) and differential thermal analyses (DTA). The TGA results showed a higher thermal stability when nanoparticles are added to the polymer. Indeed, the starting decomposition temperature was increased by 30 °C and a considerable amount of residue was noticed for nanocomposite fiber. Concerning the analysis of the DTA curves the authors concluded that $Mg(OH)_2$ could act as shield to heat and oxygen because of the shift toward higher temperature of the oxidative as well as combustion exothermic peak. They referred to conventional mechanism and mode of action of metal hydroxides, i.e.: these species decompose under the form of metallic oxide at high temperature, release water and thus reduce the heat and the temperature from the material and dilute the concentration of flammable vapor and oxygen. Based on these results, they assumed that the flammability of the UHMWPE fiber can be largely reduced.

6.4.1.2 Polyamides

For the first time the fire behavior of a knitted structure made with nanocomposites multifilament yarn (80 monofilaments) was investigated in our laboratory [87]. To do this, multifilament yarn was produced by melt-spinning a compound of polyamide 6 (PA6) filled with an organo-modified clay (Cloisite® 30B, Southern Clay Products). The fire properties of textile fabrics having an area density of 1,020 g/m^2 and thickness 2.5 mm were evaluated with a cone calorimeter under a heat flux of 35 kW/m^2. It was first seen that the ignition of the nanocomposite material starts 50 s before the virgin material. Furthermore, although the values of total heat release (THR) was not specified, it can be estimated by comparing the non-common areas under the HRR curves recorded during the experiments that PA6 nanocomposite has more or less an equivalent THR to that of PA6. However, other promising results suggesting a modification of the burning behavior were obtained for nanocomposite fabric. Indeed, a sharply decrease of the volume of smoke production as well as the carbon monoxide or carbon dioxide generated during the combustion were measured. A decrease about 40 % of the peak of heat release rate in comparison of pure PA6 was also recorded in presence of clay. Moreover, a better char layer (more uniform and without holes) was also observed for PA6 nanocomposite fabric. This higher char formation was also achieved by McCord et al. during burn tests conducted on polyamide 6 and polyamide 12 filaments containing clay [88]. Various parameters involved in the formation of this protective char layer were also studied by Shanmuganthan et al. [89]. PA6/organoclay nanocomposite fibers were also prepared by spinning melt-pre-compounded PA6 with 8 wt% of montmorillonite modified with methyl dihydroxyethyl hydrogenated tallow ammonium. Then, single jersey fabrics were produced with a thickness less than 1 mm and different tightness factor by using drawn or undrawn multifilament yarns (26 monofilaments) and different stitch density on a circular knitting machine. Horizontal flame spread test and cone calorimeter experiments were performed to determine the impact of this nanofiller on the combustion of PA6 fabrics. The authors concluded that the inclusion of clays and fabric tightness factor play crucial roles in flame-retardancy behavior. Indeed, from the first method of characterization, they noticed that nanocomposite fabrics exhibited a decrease of dripping for those with low tightness factor and even an elimination of drops for those with high tightness factor. However, the ignition and the flame spreading are not significantly modified by the presence of clay. Various observations were made during the cone calorimeter experiments under a heat flux of 35 kW/m^2. First of all, a significant decrease of HRR (28 and 40 %) was noticed for samples containing montmorillonite. This trend was also more pronounced for knitting fabrics with higher tightness factor. Furthermore, due to the delay of mass loss, the authors pointed out the role of clay in the formation of a surface char able to create a mass barrier.

Apart the use of layered silicate to develop PA6 nanocomposite fibers, some works from Dogan and Bayramli were performed to introduce boron phosphate (BPO_4) nanoparticles into PA6 [84]. Two different contents of BPO_4 (3 and 10 wt%)

were mixed with the polymer in a twin screw extruder. The monofilaments obtained were then drawn with a winding unit and their mechanical, thermal and fire properties were characterized. Based on the micro combustion calorimeter results, it can be concluded that the addition of these nanoparticles changes very slightly the PHRR as well as the THR. Indeed, the reduction doesn't exceed 12 and 9 % for each parameter respectively.

Recently, there were some studies made on the production of fire retardant PA6 nanocomposite fibers by dispersing clay into appropriate solvent and by using electrospinning device. Thus, Cai et al. have produced PA6 electrospun nanofiber loaded with 4 wt% of Fe-montmorillonite which were subjected to thermogravimetric analyses (TGA) as well as carbonization experiment by using a tube-furnace in order to study the catalyzing carbonization effect of the filler on the matrix [90]. The collected results showed an increase of charring capacity in presence of clay at the end of TGA under nitrogen. This improvement of the thermal stability of PA6 fibers is assumed by Cai and co-workers to be a consequence of different mechanisms. On one hand, they reported that some transition metal as well as degradation products coming from the decomposition of alkylammonium cations in organo-modified montmorillonite following the Hofmann elimination reaction could promote an increase of molecular crosslinking. On other hand, they suggested that the clay layers play a key role in the formation of a charred ceramic surface which confines the pyrolysis products derived from polymer chain scission and lead finally to their graphitization. This presence of graphite sheets in the residue has been confirmed by X-ray diffraction, high resolution transmission electron microscopy, selected-area electron diffraction and laser raman spectroscopy. In a parallel publication, this research team has characterized respectively by TGA and Micro Combustion Calorimeter (MCC) the thermal stability and the flammability behavior of such PA6/organic-modified Fe-montmorillonite nanofiber as well as same fibers coated by silicon nanoparticles [91]. As seen for fibers filled with nanoclay, the TGA results revealed an improvement of the thermal stability of the coated nanocomposite fibers. One again, this better property was attributed by researchers to the aforementioned mechanisms (protective barriers of silicate clay layers, catalysis effect of Fe^{3+}, etc.). In the case of coated nanocomposite fibers, the authors also proposed an additional mechanism to explain this increased thermal stability. The improvement of charring ability was assigned to the silicon dioxide generated by hydrolysis of tetrachloride silicone resulting from the reaction between metal halide and silicon. In MCC experiments, nanocomposites fibers with 4 wt% of Fe-montmorillonite exhibited shorter time to ignition and higher initial heat release rate than unfilled fibers. This could be due to the thermal degradation of cationic surfactants of the clay. Furthermore, fibers containing montmorillonite have a reduced peak of heat release rate compared with pure or coated PA6 (~15–19 % less). The combination of clay and silicon nanoparticles reduces this value by 25 % in comparison of virgin polymer. This improved flame retardant function was attributed to the in situ generated silicon dioxide, barrier effects of silicate clay and the synergistic effects between the clay and silicon. Other synergisms between different nanoparticles or flame retardant additives were also highlighted [92–96]. Wu showed for example that non-halogenated flame retardant additive (Exolit® OP1312, Clariant Ltd) and natural montmorillonite modified with a quaternary ammonium salt (Cloisite® 30B, Southern Clay Products) could effectively improve flame retardant properties of the material in fiber form as well as in bulk form. Thus, electrospun formulation with 2.5 wt% of montmorillonite and 10 wt% of flame retardant additive achieved a significant decrease in heat release capacity (more than 15 %) during MCC experiments. In other recent work, electrospun polyamide/boric acid nanocomposite fibers were used to confer flame-retarding property to textile material [97]. In this study, Selvakumar and co-workers showed that cotton fabrics coated with PA6 nanoweb containing different level of nanoparticles had a higher fire-spreading time and could have a 38 % increase in char formation as demonstrated by TGA.

6.4.1.3 Polyesters

To the best of our knowledge, the first developments of fire retardant polyester based nanocomposite fibers were published by members of our research laboratory. Thus, Solarski and co-workers introduced up to 4 wt% of Cloisite® 30B by melt blending into polylactide matrix before the spinning of these compounds to produce multifilaments yarns. After this, the yarns were used to knit textile surfaces (surface weight of 1,000 g/m^2 and thickness of 3 mm) which were subjected to cone calorimeter test at 35 kW/m^2. From these experiments, it can be concluded that this organo-modified clay modified the burning behavior of polylactid fabrics and encouraged some char formation. Indeed, an increase char yields as well as a strong decrease of the PHRR was recorded. However, although only 2 wt% of this layered silicate was enough to reduce the PHRR, it didn't prevent a reduction of the time to ignition as mentioned in previous study made on PA6 [87]. In subsequent work, by adopting the same protocol the authors evaluated another clay nanoparticle, i.e.: bentonite (Bentone 104, Elementis Specialties) [98]. An analysis of these two studies supports the same conclusions, i.e.: a reduction of time to ignition and of the PHRR. Nevertheless, it appears also the bentonite is more effective in reducing the PHRR. Indeed, the maximal values of HRR are 163 and 143 kW/m^2 for PLA knitted fabrics containing respectively 2 wt% of C30B and 4 wt% of bentone 104, which represents a reduction of 38 and 46 % compared to unfilled PLA fabric. Furthermore, although the THR values were not mentioned in these papers, it is obvious that the addition of C30B or bentone 104 allows a clear diminution of this parameter. Other work on the use of clay for developing effective flame retardant polyester fiber was made by Teli and Kale [99]. In this study, PET nanocomposite fibers were spun by adding master batches of linear low-density polyethylene (LLDPE) loaded with Montmorillonite (MMT) nanoclay after compatibilizing the PET and LLDPE. Given the LOI results obtained on PET/nanoclay composite made from compression molding of PET fibers, it can be suggested that the sample is flame retardant. Indeed, the LOI value increased continuously from about 20 % for neat sample to 27 % for sample containing 2 wt% of nanoclay. LOI tests were also made after the dyeing of nancomposite fibers and a slight decrease of the different recorded values was observed and attributed to the leaching of the nanofiller present on the surface of the fiber during the finishing process.

As mentioned in different works, the research of synergy between additives seems to be an interesting way to improve the fire resistance of textiles based on polymers. Thus, recent works were done by our co-workers on fibrous materials containing a mix of phosphorous-containing additives (Exolit OP1230, Clariant) and two different POSS (OM-POSS: OctaMethyl POSS and DP-POSS: DodecaPhenyl POSS) [100]. Fire properties of knitted fabrics (area density of 1,300 g/m^2 and thickness 2 mm) made from multifilaments yarns produced by melt spinning various formulations of PET filled with POSS and Exolit OP1230 were characterized by UL-94. According to the results, the neat PET specimen failed due to a complete burning and the fall flaming particles whereas all knitted fabrics made with nanocomposite filaments passed successfully this fire test. Indeed, they were classified V-2, whether the sample containing 10 wt% of aluminium phosphinate or samples loaded with 9 wt% of POSS (OM-POSS or DP-POSS) and 1 wt% of phosphorous additive. The major difference of unfilled and filled sample is that the later showed a high reduction of the dripping. In order to have more details on the combustion, cone calorimeter experiments were performed on a superposition of three knitted fabrics under an external heat flux of 25 kW/m^2. The introduction of aluminium phosphinate leads to a relevant effect on the flame retardant properties of the PET. It is pointed out by an increase of the time to ignition from 363 to 586 s for PET and PET containing 10 wt% of Exolit OP1230. However, no significant modification of the PHRR and THR was observed when this phosphorous specie was added alone. This was totally different when 1 wt% of POSS was introduced in combination with 9 wt% of aluminium phosphinate. High decreases of PHRR and THR were recorded whatever the kind of POSS. Nevertheless, the strongest reductions in term of PHRR (49 %) and THR (38 %) were observed for OM-POSS. The authors assumed that is due to an early development of an intumescent shield. In a subsequent work, they investigated the effect of introducing another kind of phosphinate, i.e.: zinc phosphinate (Exolit OP950, Clariant) with OM-POSS [101]. Contrary to the results obtained with the aluminium phosphinate, the addition of 10 wt% of zinc phosphinate decreased significantly the PHRR (43 %) and the THR (46 %), whereas a substitution of 1 wt% of phosphinate by 1 wt% of OM-POSS didn't confer superior fire retardant properties but acted negatively on the burning behavior as indicated by a higher PHRR than fabrics containing only zinc phosphinate. Although, this study revealed that zinc-phosphinate and OM-POSS were bad candidates to create a synergy able to decrease the heat evolved during a fire, it seems that they form a good pair to decrease the toxicity and the release of fumes. Analogous studies on the combined use of metal phosphinate and clay were carried out respectively by Alongi [102] and Dogan et al. [103]. In the first publication, cone calorimeter experiments made on fabrics produced with filaments containing 0.5 wt% inorganic content revealed that the combination of zinc phosphinate and organo-modified sepiolite is very effective in decreasing the PHRR (42 %) without affect negatively the time to ignition. Furthermore, noticeable improvement of the LOI was detected (from 22 % for neat PET to 31 % for PET filled with zinc phosphinate/sepiolite system). Based on these two characterizations, it also appears that the PET textile fabric developed with these functionalized nanoparticles and phosphinate is more interesting than the commercial fire retarded PET textile evaluated. In the later publication, Dogan and co-workers observed also during MCC test a high decrease of PHRR (62 %) in presence of zinc phosphinate (Exolit OP950, Clariant) and clay (Cloisite30B, Southern Clay Products). However, this reduction is not accompanied by a decrease of THR. Thus, the authors have drawn similar conclusions to those of previous studies which mentioned that the barrier structure created with plate-like nanoclays is able to slow down the escape of the flammable volatiles generated during combustion without allowing the creation of an “impermeable shield”.

In recent works, other nanoparticles were investigated in order to improve the flame retardancy of PET. Thus, Cai et al. developed ultrafine composite fibers consisting of lauric acid (LA), PET, and silica nanoparticles via electrospinning [104]. The combustion properties of composite fibers with varied amounts of nano-SiO_2 were characterized by MCC. The collected results showed that the heat resistance effect and/or barrier property generated by nano-SiO_2 resulted in an increase of initial combustion temperature and a decrease of the heat release rate for the electrospun ultrafine composite fibers. Meanwhile, Alongi and Frache reported the compounding of PET with carbon-nanofiber [105] and expandable graphite (EG) with various montmorillonite (unmodified Cloisite® NA, Cloisite® 10A and Cloisite® 30B, Southern Clay Products) [106]. For these two studies, as the study on the synergy between zinc phosphinate and POSS nanoparticles [102], they produced filaments (173.5 dTex/f48) by melt spinning, knitted textile fabrics (152 g/m^2) and evaluated their combustion by cone calorimetry under a heat flux of 35 kW/m^2. The cone data from the fabrics showed that the time to ignition was never improved when nanoparticles were added. It can also be noticed that PHRR values were almost the same for samples containing zinc phosphinate/clay combination (PHRR $= 292 \pm 15$ kW/m^2) and those filled with 0.5 wt% of carbon nanofiber (PHRR $= 288 \pm 31$ kW/m^2 or 282 ± 28 kW/m^2 depending of the purity of nanofiber). Regarding all the results, the highest reductions of PHRR were obtained for knitted fabrics with lower content filler in clay and expandable graphite (EG), i.e.: with 0.25 wt% of unmodified cloisite (58 % reduction) or 0.25 wt% of EG (82 % reduction). In this latter study, it can also be highlighted that the synergy observed between EG and cloisite in bulk PET was not shown for PET in fibrous form.

6.4.1.4 Other Fibers

Among the research conducted on the development of nanocomposite fibers based on polymers other than polyolefins, polyamides and polyesters, it may be first mentioned the work done by Horrocks et al. on polyacrylonitrile [107]. In this study, they incorporated nanoclay (various nanoparticles supplied by Southern Clay Products) either during the polymerization of the acrylic monomers or directly during a blending with a commercial polymer solution. After that, the composite polymer samples prepared from polymerization or from the commercial formulation were spun via a conventional wet-spun process. All filaments produced were collected as continuous tows and kept wet by using water before to place them in a soluble APP product (Antiblaze LR2, Rhodia Consumer Specialties). From the various experiments, the researchers showed the ability of filaments to absorb water-soluble flame retardant. Furthermore, a synergy between phyllosilicate clay and an ammonium polyphosphate was clearly demonstrated by LOI characterizations and calculation of $\Delta\mathrm{LOI}_{\mathrm{nano(corr)}},$ which relate only to the effect of the clay. Thus, the authors demonstrated an increase of 4.2 of this LOI value when 1 wt% of clay was added and concluded that the use of clay is an interesting way to decrease the content of flame retardant while keeping the same degree of flame retardancy. However, they noted one last challenge, which is how to avoid the removal of APP during washing.

Due to the specific properties of nanofibers and their uses in wide technical applications, some studies dedicated to the improvement of their fire properties can be found in the literature. Thus, Cai et al. investigated by MCC the effect of $FeCl_3$ on the combustion property of polyacrylonitrile nanocomposite fibers prepared by electrospinning [108]. Based on these tests, it was found that the addition of $FeCl_3$ induced the macroradicals recombination and intermolecular crosslinking via gas-phase flame retardant mechanism, and decreased distinctly the PHRR, which contributed to the improved combustion property of composite nanofibers. Other studies reported better flame retardation of nanofibers containing various layered silicate. Wang et al. showed by TGA an increase of char formation and consequently a potential flammability reduction when a montmorillonite or a synthetic, layered magnesium silicate was added to fibers of poly(MMA-co-MMA) copolymers [109] whereas Yacoob et al. demonstrated that electrospun PVA/Laponite had slower burning rate than that of pure PVA [110].

Among all previously quoted fibers, a last class of fibers can be added, i.e.: the thermostable fibers. These fibers, which can withstand high temperatures for more or less long periods without losing their mechanical properties, can be used in hi-tech sectors where improved fire properties are required. Thus, some authors have tried to extend this property by adding nanoparticles. Gladunova et al. introduced brominated and chlorinated phthalocyanine, and carbon black nano-additives at 2–5 wt% in polyoxadiazole fibers and evaluated particularly their oxygen index [111]. The authors demonstrated that the use of these additives leads to obtain filaments having oxygen index up to 34 %. As for Janowska et al., they highlighted that woven fabrics made from polyimidoamide containing 3 wt% of various montmorillonite nanoparticles can be considered as flame-retardant fibers [112, 113].

6.4.2 Surface Treatment and Coating

6.4.2.1 Nanocoating

Nanocoating such as back coating, corresponding to the addition of a small amount of nanometers filler in a coating formulation, allows to enhance the durability of the treated fabric. Therefore, as underlined by Bourbgot et al. the inclusion of nanoclay and POSS in polyurethane coating applied to PES and cotton allows the reduction of peak heat release [114]. Wang et al. have investigates the incorporation of layer double hydroxides and nanometer titanium to polyphosphate-pentaerythritol-melamine coating, which allows to enhance the resistance of the coating [115].

Nanocoatings is also described as surface engineering processes by physical methods have attracted considerable attention, since they allow atomistic or molecular deposition films less than 100 nm of thickness from environmentally friendly technologies. Many techniques are used to accomplish the atomistic/molecular deposition such as physical vapor deposition (PVD), chemical vapor deposition (CVD), electro platting or electroless plating, laser vaporization, plasma deposition or plasma-based CVD to realized film deposition, etc.

The sputtering technology is used to realize very thin films on the nanocomposite fibers. Cai et al. have prepared PA6 nanofibers with organic-modified Fe-montmorillonite nanocomposites and coated by silicon nanoparticles using magnetron sputter technique [91]. They found that this treatment contributes to the improved flame retardant properties.

Plasma technologies achieved in different atmospheric conditions, either low or atmospheric pressure, under various types of power, are widely used in textile either to modify the structure of the surface or to depose nanocomposites into the surface. Pappas gives a clear overview of the status of nanocoatings from atmospheric plasma [116]. The excellent adhesion of these coatings to the material substrate and the cost-effective continuous process operation are the main elements that make these coatings so interesting. Dineff et al. were the first to suggest that non-halogenated flame retardant coatings from atmospheric plasma could be the solution for the existing adhesion problems with non-halogenated flame retardant coatings [117]. Furthermore, coatings from nanoparticle adsorption after plasma pre-treatments can also be used to enhance the flame retardancy properties of PET, and cotton fabrics [118–121]. The coatings showed significant flame retardant effects and very good levels of durability of the coating [121]. The results are very promising; nevertheless the flame retardant effects achieved are still far off from the required level. Main reason is that no dedicated precursors/materials for flame retardants are available for this method yet.

6.4.2.2 Nanofinishing: Sol-Gel

Sol-gel technology represents a new approach to functionalize fiber for the preparation of composite materials. This process allows the creation of nanocomposite films of functional coating on the surface of the fibers leading to new mechanical, electrical, biological and fire retardancy properties which cannot be achieved using convention finishing treatment [122, 123]. Sol-gel process is a very attractive way to gain new functionality to textile, since the small particle diameter offers the advantage to form a transparent layer, which is stable against light, heat, chemical and microbial attacks, and it improves the mechanical properties of the fabric. Furthermore, additives can be embedded in the coating and conventional process such as a pad-dry-cure method which consists of the impregnation of the textile substrate by the sol following by a drying and a curing step under appropriate conditions is used to apply the solution prepared at room temperature and normal pressure.

A sol-gel process implies the preparation of an inorganic networks through the formation of a colloidal suspension also called ‘sol’ by either acid or alkali catalyzed hydrolysis of silicon, metal alkoxides or organometallic compounds as precursor, and the gelation of this ‘sol’ to form a network. Thus, during the textiles treatment, nanoparticles condensate and aggregate on the textile surface to create a 3-D network layer and during the drying, the liquid phase containing in the cross-linked lyogel is removed to obtain a xerogel or porous layer. In the last step, the curing temperature, between 100 and 170 °C, and time, from 1 to 30 min, should be adapted with regard to the type of textile coated as well as to the applied nanosol coating to avoid any degradation [124–126].

The uses of inorganic nanosol which are inflammable are not expected to increase the flammability of the textile substrate. Therefore, for a flame retardancy application, these coatings protect the textile substrate with the creation of a physical barrier acting as an insulator, which improve the flame retardant properties and the combustion behavior of the treated surface. Thus few research groups have demonstrated that the sol-gel method improves the flame retardancy of the textile substrates in recent years [127–139]. Furthermore, the effectiveness of the thermal shielding ability is in most of case limited due to the thickness of the coating and the porosity of the xerogel which cannot act as a sufficient oxygen barrier [140]. The application of nanosol to enhance fire resistance in the textile field was only studied in the early 2000s with the use of fluorinated silane for nylon carpet, $TiCl_4$-NH_4HF_2 in dicarboxylic acid solution for wool [141]. It was also recognized in the literature that nanosols from SiO_2 have a flame retardant activity which depends on the thickness of the coating layer [129, 142]. A thinner layer is less porous than a thicker and leads to better flame retardancy properties. Tetraethyl orthosilicate (TOES) and tetramethyl orthosilicate (TMOS) have been widely used as precursors in order to enhance flame retardancy properties of viscose fibers [129], cotton-polyester blend [132] with also the aim to optimize the sol-gel process conditions. Furthermore, the sol-gel methods for textiles is not restricted in the use of silane derivative, since Alongi et al. have reported that the flame retardancy properties of cotton can be enhanced by using alumina, titania or zirconia alkoxides even if the best performances were also achieved by the silica coating on a cotton substrate [139].

Since the inorganic protective layer acts only in the condensed phase, they are suitable to interact with the release gases and smoke. Therefore, hybrid layer with active species such as phosphorus and/or nitrogen should be exploited to bring up synergistic effect [127]. Thus, a possible way to improve flame resistance is the formulation of nanosol coatings with phosphorus containing flame retardant and observed by Chapple and Ferg [143], even if this protective property decreases after rinsing due to the water leaching, and the no-covalent bonding between the phosphorous compounds and the nanosol coating. Nevertheless, the use of phosphorus hybrid as presented by Chiang et al. [144] can increase the char yield when it is introduced in epoxy. More recently, phosphorus-doped silica has been studied by Cireli et al. [128] and Brancatelli et al. [131] who added nitrogen compounds. In each case, they observed an enhancement of char-forming properties due to the synergistic effects between phosphorus and nitrogen with the silica layer. These researches were also expanded to the use of various phosphorus based compounds such as aluminium phosphinate, mixture of aluminium phosphinate, melamine polyphosphate and zinc and boron oxide, and alpha-zirconium dihydrogen phosphate. Alongi et al. have observed that the flame retardancy of cotton can be enhanced with a least 5 wt% of phosphorus compounds with respect to the sol-gel precursor [136]. They also worked for obtaining hybrid phosphorus-doped silica from diéthylphosphatoethyltriethoxysilane [137]. All these studied show that the sol-gel process is potentially interesting to enhance flame retardancy properties of cellulosic substrates and the possibility to design the coating layer in order to research synergistic effects.

6.4.2.3 Nanofinishing: Layer-by-Layer (LBL) Technique

Initially discovered by Iler in 1966 [145], and thereafter developed by Decher and Hong in the 90s [146], layer-by-layer technique has become a popular method to realize multifunctional coating with a thickness less than 1 μm [147]. The resulting films are used in various fields to impart oxygen barrier [148], anti-reflection [149], electrical conductivity [150], antibacterial properties [151], drug delivery [152, 153] and more recently to design flame retardant coatings [148, 154–163]. The main advantages of this technique include simplicity, universality and the control of the thickness at the nanoscale level, compared with the other traditional coating. Furthermore, it is possible to combine nanoparticles, nanosheets as well as nanowires with polymers.

Layer-by-Layer (LbL) assembly consists in the deposition of oppositely charged polyelectrolyte multilayer films onto the surface of a substrate. The self-assembly process is based on spraying or immersion (dipping method) of a charged surface in polyelectrolyte solutions followed by a rinse in water to remove surplus polymer solution adhering to the support. This technique of polymer thin film deposition allows creating uniform film with a controllable thickness. Assemblies are done through electrostatic interactions, donor/acceptor interactions, hydrogen bonding, and covalent bond. The process is mainly influenced by the chemical nature and the chemistry of the polyelectrolyte, the molecular weight, the temperature and pH, and the ionic strength as well as the presence of the counterions. This coating method has received growing interest in the last decade and various organic of inorganic molecules can be deposited to bring new functionalities to the resulting film.

In textile application, the fabric (cotton, PET, ramie, …) was first immersed into the cationic solution for 30 s to several minutes, washed with deionized water or buffer solution, generally dried with air before being immersed into the ionic solution for 30 s to several minutes, washed with deionized water or buffer solution and dried with air to build the first bilayer architecture. The immersion period for this bilayer is optimized to promote and achieve the uniformity and stability of the coating. Thereafter the procedure was repeated until the desired number of bilayer was obtained. Finally the treated fabrics were dried under vacuum or in an oven to complete water evaporation.

According the chemical nature of the textile fabrics several strategies have been explored. Thus, to enhance flame retardancy properties of cotton fabrics, Grunlan et al. have used a branched polyethylenimine as cationic specie couples to laponite [162], sodium cloisite [161], silica nanoparticles [159] or polyhedral oligomeric silsesquioxanes [160]. Huang et al. have selected poly(acrylic acid)/montmorillonite and polyacrylamide/exfoliated grapheme oxide couples to reduce the flammability of cotton [164, 165]. Carosio et al. have investigated the PET coating from colloidal alumina/coated silica with silica [154], α-zirconium phosphate/polydia llyldimethylammonium chloride as cationic polyelectrolyte [158]. For polyester/cotton blends, Alongi et al. have realized complex architecture from ammonium polyphosphate, chitosan and silica [166]. The results of the fire tests conducted on these fabrics seems very promising since in all cases it was observed a significant improvement of their thermal stability, an increase of the time to ignition, and a decrease of the heat release rate.

6.4.2.4 Nanomaterials Embedded Textile

To improve the washing durability, nanomaterials can be fixed into the textile fabric. One of the methods to embed nanoparticles is to use a cross-linking agent or crosslinkable polymeric binders such as polysiloxane or carboxylic acid for carbon nanotube (MWCNT), silver particle or fumed silica. Another way is to realize the in situ synthesis of these nanoparticles such as a bottom up process. Thus, it was shown that MWCNTs improve thermal stability and provide a char barrier, these particles are incorporate into the fabrics using a process that mirrors industrial methods [167].

Nano rods can grow on any substrate by two ways. Firstly, the substrate is seeding with nano seeds and growth of nano rods by hydrothermal process. These nano seeds provide site for nucleation of nano rods [168–172]. Secondly, growth of nano rods on self-assembled monolayer (SAM) modified surface [173, 174]. Most of the time, a straightforward approach is to seed the substrate with nanoparticles of the desired material by different techniques, such as dip coating or sol-gel coating. Once the seed layer is formed, oriented nanocrystals growth follows in a second step. In order to attach seeds on any surface, presence of polar groups on surface is very essential. Therefore different methods have been used to generate (UV treatment, sodium hydroxide). Oriented nanocrystals grow from these nucleation sites, and in subsequent reaction steps, new crystals nucleate and grow on the crystals produced in previous stages. So the initial nano rods formed at the surface can be converted into other forms (flowers) by using a secondary growth [175].

6.5 Conclusion

Economic, environmental, legal constraints make that research on the fire resistance of textiles is still relevant. Among the various ways of improvement, nanotechnology has been and remains a relevant possibility. This chapter presented the various nanotechnologies that have been tried to provide fire retardant properties. Nanotechnologies for textile are found either in the process of yarns or through surface treatment and coating.

Regarding the spinning, the most widely used synthetic fibers (PP, PET, PA) were studied with a wide range of nanofillers. Overall the presence of nanofillers even low rates reduces during heat/fire stress the phenomenon of melt dripping and the peak of heat release rate. However the charring effect is often insufficient with e.g. a total heat release equivalent to the untreated fiber. This feature already observed for the bulk polymers is even more pronounced for the same polymers in a fibrous state. Nanofillers were also associated with the traditional FR agents. Results are disparate where a synergistic effect has been observed only sometimes.

Except coatings containing nanofillers and plasma process (technologies already since 10 years in textile), surface treatments based on sol-gel and layer-by-layer techniques are much more recent and show the most promise for FR properties. These techniques seem to have low cost and environmental impact and to adapt to all sorts of fabrics (polymeric nature). Initial results are encouraging and demonstrate synergies with traditional FR compounds.

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Chapter 7
Flame Retardants in Bitumens and Nanocomposites

Henglong L. Zhang, Jianying Y. Yu and Chongzheng Z. Zhu

Abstract To realize the flame retardant of bitumens correctly is of great significance for academicians and technicians. This chapter begins by introducing the types and properties of conventional flame retardants modified bitumen. It then based on exist disadvantages of conventional flame retardants modified bitumen, further introduces environmental friendly flame retardants using in bitumen and bitumen/flame retardants nanocomposites. The chapter finally outlines a short commentary on likely future trends and provides some sources of further information and advice.

Keywords Bitumen · Flame retardant · Conventional flame retardant · Environmental friendly flame retardant · Nanocomposites

7.1 Introduction

Bitumen is widely used in many aspects of infrastructural construction, such as in pavements, waterproofing and protective coats. One of the most important uses of bitumen is for pavement construction due to their excellent road performance, such as driving comfort and safety, low noise levels, fast construction, and easy maintenance, etc. However, bitumen is partially composed of hydrocarbon materials, its pyrolysis and combustion in a tunnel traffic easily release plenty of poisonous smoke and toxic gases in a short time [1], which will not only cause a serious threat to people's life and property security, but also prevent its widely used in road tunnel. Nowadays tunnel fire is an international problem, and many countries of the world have been appearing

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very serious tunnel fire. Therefore, the flame retardancy of bitumens proposed for tunnel pavements is an increasingly important research consideration [2–4].

This chapter, for this purpose, firstly introduces the types and properties of conventional flame retardants modified bitumen. Secondly based on existed disadvantages of conventional flame retardants modified bitumen, further introduces environmental friendly flame retardants using in bitumen and bitumen/flame retardants nanocomposites, moreover a short commentary on likely future trends is also contained in this chapter.

7.2 Conventional Flame Retardants Modified Bitumen

In this section, the types and properties, the flame retardant mechanism and the test methods of conventional flame retardants modified bitumen are introduced.

7.2.1 The Types and Properties of Conventional Flame Retardants Modified Bitumen

Conventional flame retardants can be classified into five main types: halogen flame retardant, phosphorous flame retardant, mineral fillers flame retardant, boron flame retardant and antimony flame retardant.

7.2.1.1 Halogenated Flame Retardant

Chlorine and bromine are the main types of halogenated flame retardants. Halogenated flame retardants which operate in the gas phase, by replacing the free radicals ($OH^\bullet$ and $H^\bullet$) responsible for flame propagation with more stable species, such as chlorine and bromine anions, able to stop the combustion reaction, significant enhancement of bitumen's flammability was achieved [1, 5, 6]. These act primarily by chemical interference with the radical chain mechanism (as per Eqs. 7.1–7.4) in the gas phase during combustion. However, some important drawbacks existence, like the formation of smoky, toxic and corrosive effluents hindered the development of halogenated flame retardant.

$$RX \rightarrow R^\bullet + X^\bullet \tag{7.1}$$

$$X^\bullet + RH \rightarrow R^\bullet + HX \tag{7.2}$$

$$HX + H^\bullet \rightarrow H2 + X^\bullet \tag{7.3}$$

$$HX + OH^\bullet \rightarrow H2O + X^\bullet \tag{7.4}$$

RX is a hydrocarbon halide.

7.2.1.2 Phosphorous Flame Retardant

The most widely marketed and available non-halogenated alternatives are based on phosphorous compounds. Common examples of this class of flame retardants include elemental red phosphorus, phosphines, phosphine oxides, phosphonium compounds, phosphonates, phosphites, phosphinates and phosphates. These compounds mostly act in the condensed phase by altering the pyrolytic path of the polymeric material and reducing the amount of gaseous combustibles (dehydration and char formation are the principle modes of action) [7]. For example, most phosphorous-based compounds are converted to phosphoric acid during thermal decomposition, which condenses to produce pyrophosphate and polyphosphate structures by elimination of water. They can catalyze the dehydration reaction of polymer end chains (and any reactive group) and trigger char formation. The released water dilutes the oxidizing gas phase. In some cases, phosphorus-based flame retardant volatilize into the gas phase to form active radicals ($PO2^\bullet$, $PO^\bullet$ and $HPO^\bullet$), and act as scavengers of $H^\bullet$ and $OH^\bullet$ radicals [8]. Some initial studies on the toxicity of phosphorous-based compounds have also pointed out that these flame retardants are neuro-toxicants after they break down in the environment. In addition, when they volatilize and condense, stress corrosion cracking of various parts can occur [9].

7.2.1.3 Mineral Fillers

Mineral fillers are composed of inorganic hydroxides and carbonates which endothermically decompose under fire conditions which cool the burning bitumens and release non-flammable gases such as water and carbon dioxide. Typical examples include aluminum and magnesium hydroxides, as well as calcium and magnesium carbonates. As the name implies, these flame retardants are typically mined from mineral deposits and used as bulk fillers in bitumens to provide fire protection. Some synthetic grades of mineral fillers exist, especially for magnesium hydroxide. These flame retardants are of great utility in bitumens formulations because they help lower heat release and smoke at the same time. However, they must be used in high loading levels in materials (>20 %, mass fraction) to impart effective flame retardancy, which have a negative impact on the performance of modified bitumens. Otherwise this class of flame retardant is used in combination with other flame retardants to help smoke release or delay time to ignition.

7.2.1.4 Boron Flame Retardant

Boron flame retardant is mainly refers to zinc borate, which has the characteristics of good thermal stability, low toxicity, smoke abatement and good synergistic effect with other flame retardants. The effect of boron flame retardant mainly is from the following aspects when it is applied to bitumen: (1) form an inorganic intumescent coating which is glass state; (2) promote the tight charring layer generation; (3) inhibit volatile combustible escape; (4) dehydrate under high temperature, with a heat absorption, foaming and diluting combustible [5, 10].

7.2.1.5 Antimony Flame Retardant

The most commonly antimony flame retardant is antimony trioxide, which has good thermal stability, low toxicity, no corrosive gas, non-volatile and not precipitation in the process of storage, and flame retardant effect durable. What's more, antimony trioxide have a good synergy with halogenated flame retardant [5, 10].

7.2.2 Flame Retardant Mechanism of Conventional Flame Retardants Modified Bitumen

Combustion and flame retardancy are a very complex process, involving a lot of influencing factors. Fundamentally speaking, flame retardancy of bitumen is to affect or interrupt some stages during the combustion process by either a physical or a chemical way. Flame-retardant mechanism can be divided into gas flame retardancy, condensed phase flame retardancy, inhibited flame retardancy, absorbed heat flame retardancy and synergistic effect.

7.2.2.1 The Gas Phase Flame Retardancy

Gas phase flame retardant mechanism is that the flame retardants release a large fire-retardant gases (H_2O, CO_2, NH_3, N_2, *etc.*) to delay or interrupt combustion reaction of combustible gas in the gas phase. The specific process is as follows: flame retardant can release a large number of flame-retardant gases, high-density steam or tiny smoke particles and so on, which dilute combustible products that generated by oxygen and combustible burning and decomposition, lower combustible gas temperature and slow down or terminate burning. Typical representative is halogenated flame retardant.

7.2.2.2 The Condensed Phase Flame Retardancy

Condensed phase mechanism is that the flame retardants delay or interrupt combustible decomposition generate combustible gases in the condensed phase, or generate some substance layer (like tight charring layer) on the bitumen surface to achieve isolation effect. The specific process is as follows: when above bitumen processing temperature and below bitumen pyrolysis temperature, flame retardants dehydration into carbon or cross linking into carbon, which convert bitumen pyrolysis process, thereby effectively reduce combustible gases generation, not only absorb heat, but also dilute combustible gases, moreover, generated carbon can cover surface of combustible achieve isolation effect.

7.2.2.3 The Inhibited Flame Retardancy

When bitumen combustion, the main fuel is oxygen instead of carbon, meanwhile bitumen combustion rate has a close relation with hydroxyl concentration. Inhibited mechanism is that flame retardant by as much as possible substitute for the hydrogen from molecular structure or add some kinds elements into bitumen to inhibit formation of hydroxyl radicals, thereby achieve flame retardant characteristics.

7.2.2.4 The Absorbed Heat Flame Retardancy

Absorbed heat mechanism is that flame retardant after thermal decomposition will generate large amounts of water which quickly is converted into water vapor to take away a lot of heat, thereby realize flame retardant. The specific process is as follows: when above bitumen processing temperature and below bitumen pyrolysis temperature, the flame retardant occurs endothermic decomposition reaction which release large amounts of water and absorb a lot of heat. In fact the flame retardant serves as two roles: on the one hand, it absorbs a lot of heat and delay combustible temperature rises, on the other hand, it dilutes combustible gases concentration. In addition, this flame retardant has high heat capacity, so may react carbonation make burning slow or even terminate.

7.2.2.5 The Synergistic Effect

The synergistic effect mechanism is that some substance may itself has not flame retardancy or poor flame retardancy, yet when used with other flame retardant can have superior flame retardant effect to a single flame retardant, the typical examples are antimony and halogen, magnesium hydroxide and aluminium trihydroxide and so on [11, 12].

7.2.3 Test Method for Conventional Flame Retardation

7.2.3.1 Oxygen Index Test [13]

Oxygen index test was first developed to quantify performance of flame for plastics (China standard, GB/T 2406-1993), fiber glass (China standard, GB/T

8924-2005), rubber (China standard, GB/T 10707-2008), textile (China standard, GB/T 5454-1997), etc. The essence for those tests is the same though there are many different procedures. Oxygen Index ("OI") could be regarded as how much O_2 content in the combined gas flow of N_2 and O_2 is needed at least to guarantee burning. It could also be called "Limit Oxygen Index" ("LOI"). OI could be represented as follows,

$$OI = \frac{[O_2]}{[O_2] + [N_2]} \times 100$$

where;

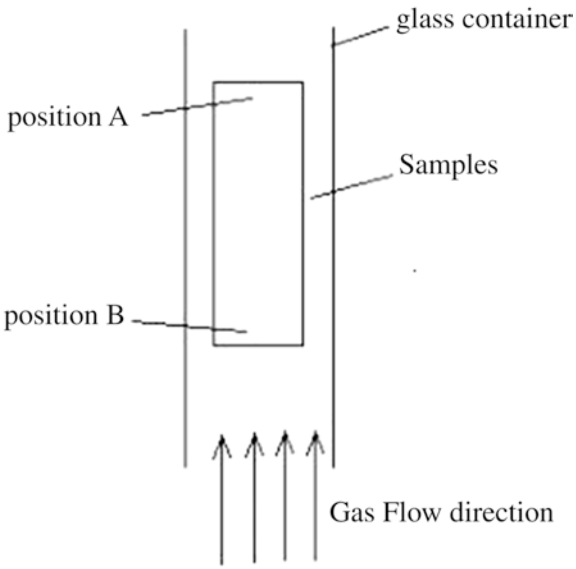
$[O_2]$ Volume Flow of O_2, L/min;
$[N_2]$ Volume Flow of N_2, L/min.

However, the test procedures are supposed to be modified based on the flame performance of the asphalt mixture. Some factors that affect the results of the test are: temperature and weight of samples before testing, volume flow of combined gases, position of burning for samples, etc.

(1) Test samples. Different types of samples were used by researchers in the "OI" test. However the heat could have affected the medium, which could influence the results. Some medium was inflammable others were flammable. Typically, in order to achieve the real performance of combustion, it is necessary to avoid the effect of the medium on results. The ideal medium would be flammable but can be put out immediately. Flammability could make the burning propagation easy which could simulate the fire in the field and, meanwhile, the fire in the medium would be extinguished as soon as possible so that it won't contribute to the bitumen burning, which might mislead results. Therefore, a polyester grid was employed in this test. Figure 7.1 is the configuration of test samples.
(2) Position of light. The fight position will have some effect on the OI results. Assuming that there is a sample in the glass container, the gas flow is showed in Fig. 7.2. Position B is at upstream while position A is at downstream. From the test, position B is vulnerable to burn as compared to position A, which

Fig. 7.1 Test samples for oxygen index [13]

Fig. 7.2 Oxygen index [13]



means the result from position B will have a lower OI than position A. Actually, position B will lead to the lowest OI in the whole sample. Considering the most unfavorable condition, position B was regarded as the test fighting position.

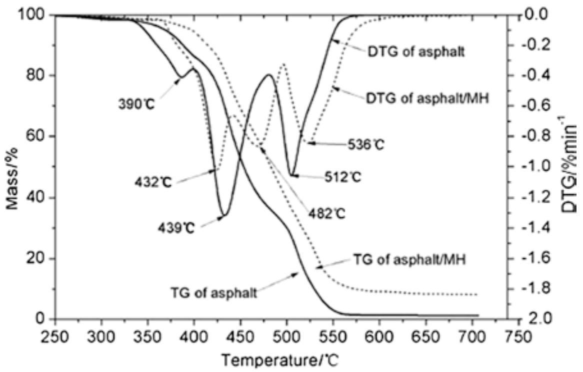
(3) Weight of sample. Weight of sample could have some effects on test results. As the sample weight is increased, it will absorb or release more energy in the process of combustion. The relationship between weight of the sample and burning time was studied in this paper at the same volume flow rate and O_2 content. Results showed that the weight of sample has no statistically significant effects on OI. The reasons for this might be the effective contact area for the sample to O_2. Based on the test results, the weigh of each sample will be round 20 g.

(4) Volume flow of combined gases. Different volume flow will cause different results in OI even for the same kind of materials. With the increase of flow rate, the propagation speed of heat rises. Then energy inside the sample won't be enough to keep the burning, which means the burning will cease. Assuming a certain weigh of sample, at the same O_2 content, the function relationship between whole volume flow rate and burning time will be a negative correlation. Therefore, the volume of flow for the combined gases should be specified.

7.2.3.2 Thermogravimetry (TG)

TG is a technique in which the mass of the sample is monitored (balance) against time or temperature (thermal) while the temperature of the sample, in a specified atmosphere, is programmed. This technique serves the determination of material compositions. It is a common analysis method in the chemical and pharmaceutical industry.

Fig. 7.3 TG–DTG curves of bitumen and bitumen/MH composite combustion [23]



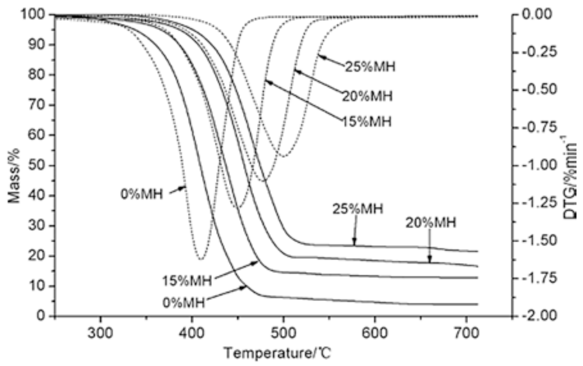
TG technique has been extensively used to study thermal degradation behaviors for many years because it is of advantage to not only better probe the chemical species ejected from the thermal degradation online [14–16], but also provide the necessary dynamics information to reveal the combustion mechanism at low heating rate [17].

Recently, many researchers have employed the experimental results of TG and derivative thermogravimetry (DTG) to illuminate increases in the thermal stability of bitumens or polymers through the addition of flame retardants [6, 18–21]. Meanwhile, thermal kinetic analysis has been used to study the pyrolysis mechanisms of different materials [16, 22]. For example, to evaluate the effect of MH on the pyrolysis behavior of the bitumen, TG experiments with the pure bitumen and bitumen/MH composite were performed in N_2. The TG and DTG curves of the bitumen and bitumen/MH composite are shown in Fig. 7.3 [23], and TG and DTG curves with different concentrations of MH are shown in Fig. 7.4 [20].

7.2.3.3 Differential Scanning Calorimetry (DSC)

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a

Fig. 7.4 TG–DTG curves of bitumen pyrolysis with different concentrations of MH [20]



function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions.

The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, depending on the kind of technology used in the experiment. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation:

$$\Delta H = KA$$

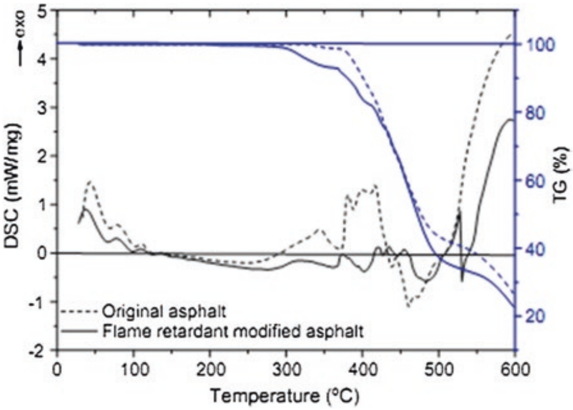


Fig. 7.5 Results of the DSC–TG test of original and flame retardant modified bitumen [5]

where ΔH is the enthalpy of transition, K is the calorimetric constant, and A is the area under the curve. The calorimetric constant will vary from instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition.

Recently, DSC were performed to studying the thermal properties of bitumen [1, 6, 19]. For example, Fig. 7.5 shows DSC–TG test results of original and flame retardant modified bitumen at a wide temperature range from 25 to 600 °C [5].

7.3 New Types of Environmental Friendly Flame Retardants Using in Bitumen

Nowadays, as people's awareness of environmental protection and safety concerns are growing, researchers have tended to develop flame retardants that are halogen-free, nontoxic, and smoke-suppressive. Much attention has been paid to halogen-free flame retardants in the past two decades [24, 25]. Based on the existed problems of conventional flame retardants modified bitumen, it is of much significance to develop new types of environmentally friendly flame retardant bitumen. Some new environmental friendly flame retardants bitumen have been developed at present, such as inorganic hydroxide flame retardant bitumen, intumescent flame retardant bitumen, nanometer flame retardant bitumen and so on.

7.3.1 Inorganic Hydroxide Flame Retardant Bitumen

Inorganic hydroxide flame retardants belong to mineral fillers, which mainly include magnesium hydroxide (MH) and aluminium trihydroxide (ATH).

MH, a kind of halogen-free flame retardant, has properties of flame retardancy, smoke suppression and does not pollute. MH has come into widespread use as a replacement for traditional halogen-containing additives. Many investigations have concentrated on the use of MH as a flame retardant [26, 27]. XU and Huang studied the smoke suppression mechanical of MH in bitumen combustion process [23]. The results showed that the combustion processes of bitumen and bitumen/MH composite are both multistage, and the volatiles are different in each temperature interval. After adding MH into bitumen, the temperature rise of bitumen matrix is inhibited due to MH thermal decomposition. Firstly, the water vapor dilutes or absorbs some carbon particles to hinder the soot nucleation and aggregation, and then smoke density is decreased. Secondly, the active magnesium oxide (MgO) promotes the tight charring layer generation on the bitumen surface. The layer hinders carbon particles and flammable volatiles from releasing out of bitumen, and the starting release time of volatiles is also deferred. The incomplete combustion residue of bitumen is absorbed by MgO to prevent droplet generation at high temperature. Also, the smoke nuclear and soot particles are reduced by the sorption of MgO. Finally, because MgO is alkaline, the acid combustion products are neutralized quickly to generate some compounds in bitumen. Because of the above effects of cooling, dilution, absorption and neutralization from MH, the purpose of smoke suppression is achieved, and the release amount of harmful volatiles is reduced, without any generation of harmful substances during bitumen combustion process. It is concluded that MH may be used as a new kind of environment-friendly and efficient smoke suppressant for bitumen.

ATH is also a kind of halogen-free and smoke-suppressive flame retardant, whose main advantage over other similar agents is its low cost and negligible toxicity. ATH on burning builds up a protective aluminum oxide layer cutting down the supply of oxygen and the decomposed organic products into combustion zone. Also, the water molecules produced of the burning surface. Both processes would retard the flame and the smoke and eventually stop the combustion [28]. There are some investigations on the use of ATH as a flame retardant in bitumen [12, 29, 30].

Qing and Shen studied optimization on flame-retarding bitumen system based on ATH and MH, the effect of different contents of ATH and MH on flame retardant properties of bitumen can be evaluated by Limit Oxygen Index testing [12]. The test results are shown in Tables 7.1, 7.2 and Figs. 7.6, 7.7. The results showed that the addition of ATH and MH can effectively improve the property of fire-retardant.

As new types of environmental friendly flame retardants, ATH and MH have vast potential for future development.

7.3.2 Intumescent Flame Retardant Bitumen

Now a kind of environmental friendly flame retardant, intumescent flame retardant (IFR) is developing at a rapid pace, whose main active components are phosphorus

Table 7.1 Flame-retarding performance of bitumen adding ATH [12]

ATH addition rate/%	Reagent		325 mesh		1250 mesh	
	LOI/%	FP/°C	LOI/%	FP/°C	LOI/%	FP/°C
0	20.8	324	20.8	324	20.8	324
10	22.3	329	22.6	336	24.6	342
20	23.7	338	25.0	343	28.4	349
30	25.4	344	26.8	348	29.6	351

Table 7.2 Flame-retarding performance of bitumen adding MH [12]

MH addition rate/%	Reagent		1250 mesh	
	LOI/%	FP/°C	LOI/%	FP/°C
0	20.8	324	20.8	324
5	22.6	326	24.4	327
10	23.4	327	25.2	329
15	24.2	326	26.1	330

Fig. 7.6 Effect on ATH for flame-retarding performance [12]

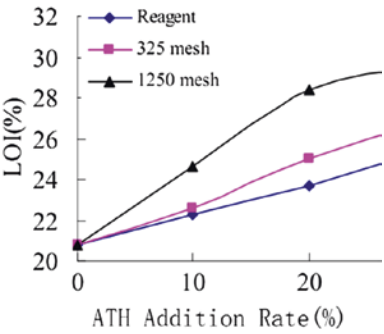
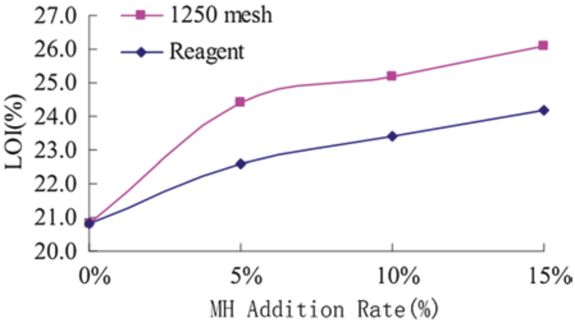


Fig. 7.7 Effect of MH for flame-retarding performance [12]



and nitrogen. It is halogen-free, efficient and smoke-suppressive flame retardant. IFR is mainly composed of acid source, carbon source and air source, which respectively act as dehydrant, carbonific and foamer. Generally, the acid source, carbon source and air source of IFR respectively are ammonium polyphosphate (APP), pentaerythritol (PE) and melamine (MA) [31–34]. The action of IFR is mainly through a condense-phase mechanism, while burning. When IFR bitumen is heated at high temperature, APP breaks up into polyphosphoric acid and ammonia. Polyphosphoric acid which is a strong dehydrant make bitumen dehydration carbonization, and the esterification reaction of polyphosphoric acid and PE further make bitumen dehydration carbonization, so the carbon layer thicken. Ammonia from decomposition of MA make carbon layer foam inflation that can insulate heat, cut off oxygen and suppress smoke, finally realize efficient flame retardant.

Intumescent flame retardants have been greatly studied for fire protection needs [35]. These flame retardants react in response to heat by forming a protective carbon foam on the surface of a material exposed to flame. They can be put directly into bitumens. Their main limitation is that they activate at temperatures below 200–240 °C, preventing their use in bitumen with high processing temperatures [36].

7.4 Bitumen/Flame Retardants Nanocomposites

7.4.1 *Introduction*

Nanocomposite technology is the newest class of flame retardant materials. As tiny particle size, nanometer has many excellent performances such as tiny size effect, surface effect, macroscopic quantum tunnel effect, etc. Therefore nanocomposites serve as flame retardants is applied to bitumen, will make its performance superior to others. Compared with the traditional flame retardants such as halogen, phosphorous and intumescent flame retardants, nanocomposites have shown dramatic improvements in the mechanical, thermal, and barrier properties with a small amount of nano flame retardants.

The present flame retarded nanocomposites can be sorted into the following three types according to the dimensionality of nanoparticles: layered materials, such as clay (e.g., montmorillonite: MMT), graphite oxide (GO) and layered doubled hydroxides (LDH), which are characterized by one nanometric dimension; fibrous materials, such as carbon nanotubes and whiskers, [37] which are characterized by elongated structures with two nanometric dimensions; particulate materials, such as aluminum hydroxide, fullerene (C60) which are characterized by three nanometric dimensions [38].

7.4.2 *Flame Retardant Mechanism of Nanometer Composite Materials*

7.4.2.1 Barrier Effect

In clay nanocomposites, the clay platelets disperse in the bitumen matrix in the intercalated multilayered or exfoliated single layered structure. The clay platelets are not totally rigid and parallel to their adjacent macromolecule chains. This special nano-structure leads to a detoured path for the small molecules to spread out when heating. This detour improves the diffusion time of degraded small molecules and thus, improves the barrier effect during combustion of materials. The X-ray photoelectron spectroscopy (XPS) investigation [39–43] reveals that in clay nanocomposites, clay breaks down and degrades into aluminosilicate and migrates to the surface. The impermanent barrier can prevent mass transport and isolate the underlying bitumen from the thermal energy. Many investigations into effect of nanocomposites on flame retardancy of bitumen have existed [29, 44].

Zhang and Shi studied effect of organic layered silicates (OLSs) on flame retardancy of bitumen [44]. The limiting oxygen index measurement has been shown in Fig. 7.8 as the function of increasing concentrations of OLSs [44]. The results showed that organic layered silicates can improve flame retardancy of bitumen because of their barrier property and expansibility. Liang and Yu also studied flammability and thermal properties of bitumen with aluminium trihydroxide and expanded vermiculite [29]. Effect of single ATH (aluminium trihydroxide) and

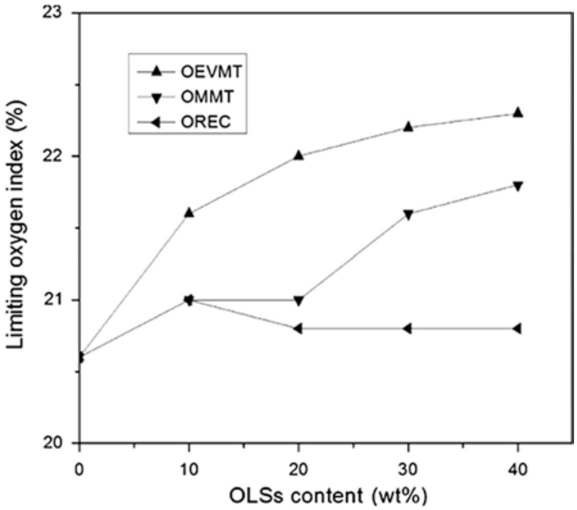


Fig. 7.8 Effect of OLSs content on LOI value of bitumen [44]

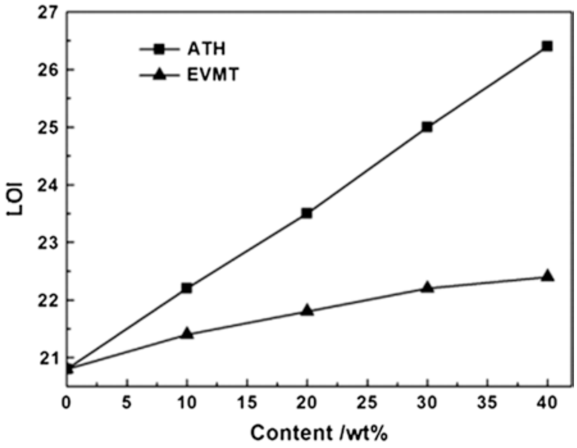


Fig. 7.9 Effect of single ATH and EVMT on LOI of the base bitumen [29]

EVMT (expanded vermiculite) on LOI of the base bitumen is shown in Fig. 7.9 [29]. The reason why EVMT has a slight inhibition on the bitumen flammability is assigned to the exfoliation and dispersion of the silicate layers which impedes heat diffusion in the bitumen molecules [44].

7.4.2.2 Network Structure and Enhanced Viscoelasticity [38]

It was proposed that a so-called three-dimensional nanofiller network structure would be formed when the content of nano-fillers reached a threshold value. The network structure can be characterized and confirmed by the dynamic viscoelastic behavior of the nanocomposites. The network structure can improve the melt viscosity of nanocomposites and confine the thermal movement of bitumen chains. Besides, the network structure can efficiently improve the barrier character to the evolution of flammable volatiles and the ingress of oxygen to the condensed phase. Therefore, flame retardancy of the nanocomposites is significantly improved. The threshold value was determined by the percentage and dispersion of the nanoparticles. The network structure can be formed only here is a suitable addition of nanoparticles and good dispersion [45]. This mechanism can be explained by referencing polymer nanocomposites. In poor dispersion conditions, the distance between nanoparticles is too far to form an efficient network structure. Because the regions between the isolated islands were exposed to an undiminished external heat flux, polymer chains without protection were burnt out quickly. Therefore, many small islands formed at the end of combustion (Fig. 7.10a). On the other hand, when the randomly placed overlapping nanoparticles exceed the critical loading, known as the percolation threshold, a network structure can be formed which can effectively restrain polymer chains' motion and cause obvious increase in melt viscosity.

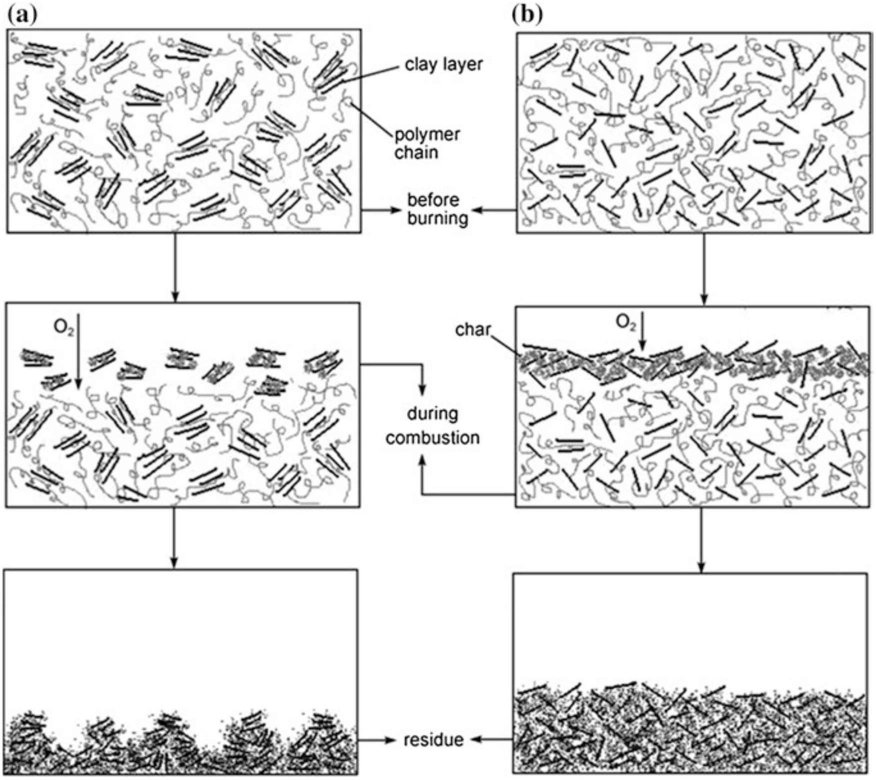


Fig. 7.10 Schematic representation of the effect of clay network structure on improving flame retardancy of ABS-g-MAH/clay nanocomposites [38]

Thick and uniform char layers were formed at the end of combustion (Fig. 7.10b). Moreover, nanoparticles such as layered silicate and carbon nanotubes act as a "sealing agent" in the final chars after combustion, leading to a more intact and compact char layer. The nano-dispersed particles can also hinder the thermal movement of bitumen chains. Due to the physical cross-linking among the nanoparticles, their nanocomposites tend to keep their original shape during combustion.

7.4.3 The Performance Assessment

7.4.3.1 Thermal Stability

Before we discuss this topic, it is important to note that improving the thermal stability of bitumen nanocomposites does not guarantee superior flame retardancy performance. The purpose is to improve the onset decomposition temperature of the system, which might influence the ignition. It is customary to modify clay layers with organic surfactants by replacing the inter-layer cations with hydrophobic cations to enhance their compatibility with bitumen. Based on the cation-exchange capacity of clay, the alkyl ammonium surfactant content in organic clay is usually over 20 wt%. But these compounds are thermally unstable and decompose, usually from 180 °C. As the processing of bitumen requires a temperature much higher than this, thermal decomposition of the organic salts is unavoidable and adversely affects the thermal stability of the nanocomposites. The decomposition (via Hoffman's elimination reaction) could also be one of the sources of fuel for ignition. In some cases, it is also noted that once the organic treatment is decomposed, the acidic site on clay surface has a direct interface with the remaining bitumen resulting in hydrocarbon cracking and/or aromatization. Though this char enhancement behavior is a positive sign for fire performance of nanocomposites, it depends on many factors, including silicate structure, acidity, etc.

7.4.3.2 Time-to-Ignition (TTI) and Thickness of Samples

According to our previous research, the flame retardance of bitumen nanocomposites depends on the TTI and thickness of samples, which is similar to that of polymer nanocomposites. Generally, for non-charring bitumen in radiative heating, it is assumed that TTI is independent of the imposed heat flux [46]. Some models correlating TTI and heat flux have also been proposed assuming no changes in the physical constants of the material prior to ignition [47]. Due to the lack of considerations such as melting/decomposition of the bitumen during heating and others including changes in the surface absorption/emission properties (affecting the heat flux), there is always uncertainty in predicting the TTI. This is particularly true for bitumen nanocomposites for which TTI is completely unpredictable and variable trends have been observed relative to neat bitumen (see for e.g. [48–51]).

But qualitatively, in most of the studies on bitumen/clay nanocomposites, an early ignition was observed for nanocomposites compared to their corresponding neat bitumen.

7.4.4 Key Technology

7.4.4.1 Investigation on Compatibility of Inorganic Nanoparticles and Bitumen

The surface of inorganic nanoparticles flame retardant is hydrophilic, while the surface of bitumen is hydrophobic, when inorganic nanoparticles is mixed with bitumen, the dispersibility will be rather poor. So it is important that change the surface property of inorganic nanoparticles flame retardant to make it has better lipophilicity. However, this makes productive process of inorganic nanoparticles complex, high-cost, so it is difficult to realize industrialization.

7.4.4.2 Dispersion-Uniformity of Nanoparticles

Nanoparticles as small particle size, big surface atomic ratio, big specific surface area, high surface energy, unstable energy state, it is easy to coagulate and reunite, then form secondary particles and generate bigger particles, finally lose the characteristics of nanoparicles. Nowadays it is important to avoid particles together, for example surfactant is effective on preventing from particles together.

7.5 Future Trends

Nanocomposites represent a relatively new technology in the field of flame retardancy. In recent years, flame retarded polymer nanocomposites as well as bitumen nanocomposites has achieved encouraging progress in both fundamental research and industrial application. However, there are still many difficulties need to be solved in this field:

(1) Present intercalating agents of clay are all highly flammable long chain alkyl quaternary ammonium salts that greatly reduce the thermal stability and flame retardancy. Moreover, due to its low stability (normally degrade at 200 °C), it is not suitable to be applied to the polymer modified bitumen. Therefore, synthesis and development of novel organic intercalating agents for the treatment of clay should be an important research area in flame retarded nanocomposites [52]. This trend is both appropriate for bitumen and polymer nanocomposites.

(2) There are still no systematically explanation of the flame retarded mechanisms for nanocomposites. Besides the barrier effect, free radical trapping and

network structure of nanoparticles mentioned above, the correlations between flame retardancy and fine structure of bitumen, varying viscoelasticity during thermal degradation and combustion need further research, which is similar to that of polymer nanocomposites [53].

(3) Although bitumen nanocomposites show significant flame retardancy, the efficiency is relatively lower than that of traditional flame retardants. Great efforts should be made to develop high-efficiency flame-retarding bitumen with new nanomaterials and/or new processing technology. These methods may increase the cost of bitumen, but it is reasonable if the new modified binders truly improve pavement performance to the degree expected.

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Chapter 8
Fire Retardant for Phase Change Material

Pongphat Sittisart and Mohammed M. Farid

Abstract Fire-retarded form-stable phase change material (PCM) products consisting of paraffin (RT21) (or propyl ester), high density polyethylene (HDPE) and fire retardants were prepared using the Brabender Plastograph. The properties of the form-stable PCM, containing different types of fire retardants such as magnesium hydroxide, aluminium hydroxide, expanded graphite (EG), ammonium polyphosphate (APP), pentaerythritol (PER) and treated montmorillonite (MMT) were classified using vertical burning test, thermogravimetry analysis (TGA) and differential scanning calorimeter (DSC). The results from the vertical burning test have shown that the form-stable PCM which contained APP + PER + MMT and APP + EG showed the best improvement in fire retardancy since it can self-extinguish by forming a large residue. The TGA graphs showed that addition of fire retardants has increased thermal stability of material by increasing the amount or residues formed, which was also supported by the Con Calorimeter testing, while DSC results showed that adding fire retardants to PCM did not change its thermal properties significantly.

8.1 Introduction

Phase change materials (PCM) are used in a wide range of applications including latent heat thermal energy storage in buildings [1]. In order for the PCMs to be used in any application, they must be encapsulated to prevent them from leaking out and hence significant research has been done in the application of form-stable PCM, where PCM is contained within the structure of polyethylene or any other polymer. One of the most suited PCM are paraffin, fatty acids and their esters

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because it has many desirable properties such as high latent heat of fusion, varied phase change temperature, negligible super cooling, and lower vapour pressure in the melt, chemically inert and stable, self-nucleating, no phase segregation and commercially available at acceptable cost [1].

Research conducted by Farid et al. [2, 3] has shown that the application of paraffin (RT20 or RT21) in building materials can provide thermal storage benefits. This is due to its desirable physical and thermal attributes including its suitable melting temperature of 20–22 °C, which is close to human comfort temperature. Experimental results based on gypsum wallboard impregnated with PCM (PCMGW) showed that, during summer, PCM can effectively reduce diurnal daily fluctuations of indoor air temperatures and maintain indoor temperature at the desired comfort level for a longer period of time. Major benefits of thermal energy storage in winter are capturing solar radiation and reducing electrical demand charges by limiting the need to run electricity for heating during peak load periods [2].

The main concern in using paraffin in building constructions is its flammability, as it can easily catch fire if not properly protected. Several methods have been attempted to reduce paraffin flammability. One method involves encapsulating it inside a composite building block and then placing the block inside a hollow container surrounded by non-combustible concrete [4]. Some have tried impregnating PCM into gypsum wallboard [5]. Others have encapsulated the PCM in polymers forming what is known as shape stabilized PCM, which could be formed to any shape for use in buildings structure and with home and office furniture. However both the polymer and PCM increase fire hazard, which require the use of suitable fire retardants [6]. The main issues in the application and use of PCM in buildings are cost and leakage. Incorporating PCM into building material will incur additional expenses. However previous study [2, 3] on the use of phase change materials showed a good potential in energy saving that may compensate for the extra cost of these materials. There is always a possibility for leakage which would render PCM unprotected during an event of fire. PCM would then become an additional fuel to the fire. In order avoid these problems two things must be done. Firstly, use a cheaper supporting material for PCM and secondly, reduce the flammability of PCM. This can be achieved by adding suitable fire retardants with the PCM into HDPE. In addition to this, low cost fire retardants should be used [6]. It must be noted that PCM could be impregnated in any building materials such as gypsum boards; however the shape stabilized PCM products have the benefit of being flexible and could be formed to any shape for use not only on building walls and ceiling but with home furniture. It is the cost of PCM, which need to be introduced before they can be applied commercially in buildings. There are approximately four types of fire retardants: flame quencher, heat absorber intumescent fire retardant (IFR) and synergist.

8.2 Types of Fire Retardant

8.2.1 Flame Quencher

The first type, and the most common, is known as flame quencher. Halogenated alkanes have the ability to limit or extinguish nearby flame source. In the presents of fire, oxide and hydroxide free radical are formed and reacts to fuels the propagation of fire. When halogenated alkanes are present, they react with oxide and hydroxide free radical to give an inactive halogen free radical. Halogen free radical is less reactive than oxide and hydroxide radical therefore its presence retards the spread of fire [7].

8.2.2 Heat Absorber

The second type is called heat absorber. Materials such as magnesium hydroxide and aluminium hydroxide, which absorb heat from the surrounding and decompose endothermically preventing nearby material from heating up and hence minimizing its combustion. The decomposing reactions are as follow:

Magnesium hydroxide decompose at 350 °C

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

The TGA graph in Fig. 8.1 shows that magnesium hydroxide starts to decompose to magnesium oxide and water at around 350 °C and finished at about 420 °C. Approximately 25 % weight loss is due to evaporation of water. The fact that magnesium hydroxide has a relatively high temperature of degradation and also a high residue at 600 °C (about 72 % residues as shown on Fig. 8.1) means that magnesium hydroxide is resistance to fire.

Aluminium Hydroxide starts to decompose at temperature above room temperature.

$$Al(OH)_3 \rightarrow Al_2O_3 + H_2O$$

The TGA graph in Fig. 8.2 shows that aluminium hydroxide starts to decompose to aluminium oxide and water when temperature increases above room temperature (approximately 50 °C) and continues to decompose until 600 °C. Approximately 34 % weight loss is due to evaporation of water. Although temperature of degradation is low, it still has a high residue at 600 °C (about 64 % residues as shown on Fig. 8.2). This indicates that aluminium hydroxide has some fire resistance.

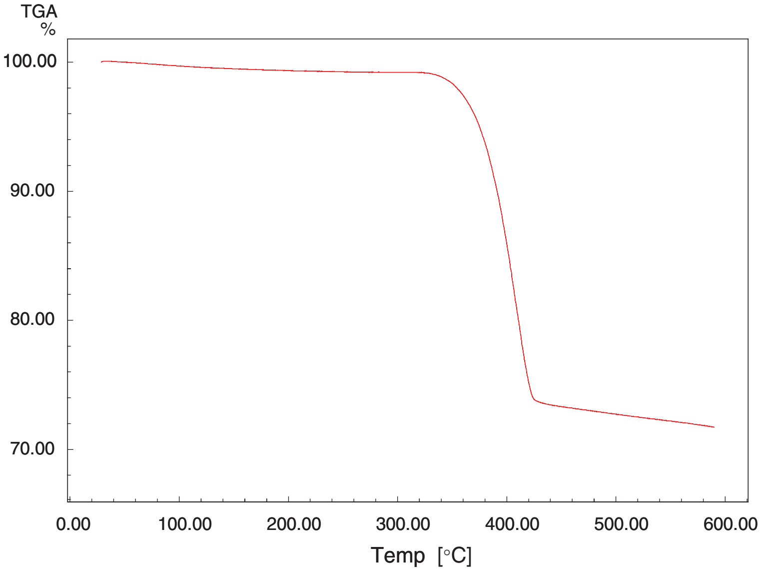

Fig. 8.1 TGA graph of magnesium hydroxide

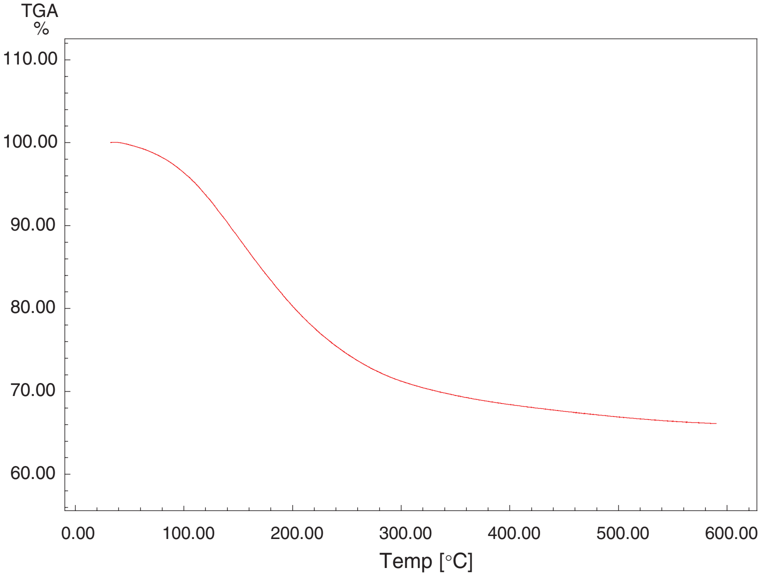

Fig. 8.2 The TGA graph of aluminium hydroxide

8.2.3 Intumescent Fire Retardant

The third type, which is relatively new, is called intumescent fire retardant (IFR). Materials such as ammonium polyphosphate (APP) + pentaerythritol (PER) or expanded graphite are common examples. IFR works by creating a voluminous char layer which prevents the underlying material from further exposure to ignition source. IFR consists of three chemicals which are: acid source such as ammonium polyphosphate (APP), carbon source such as pentaerythritol (PER) and blowing agent like melamine (MA) [8]. During heating APP decompose into polyphosphoric acid and gaseous products like water vapour and ammonia. Polyphosphoric acid then reacts with PER to produce an insulating char layer while at the same time those gaseous products and melamine cause swelling of char layer. Since APP produced blowing agents anyway (water vapour and ammonia) the addition of MA is not necessarily. This results in a formation of voluminous insulating char layer which protects the underlying material from further burning [9]. Expanded graphite (EG) also behaves in a similar way. EG consists of sulfuric acid, which is an acid source, and graphite as a carbon source [10]. Expanded graphite expands naturally on heating so blowing agent is not essential. The result is the same as the APP + PER system.

The TGA graph in Fig. 8.3 showed that the weight of expanded graphite increase with temperature. There are three possibilities which could explain the situation: first is the expansion of graphite, second is trapping of air between graphite layer and lastly an error which results from using small amount of EG

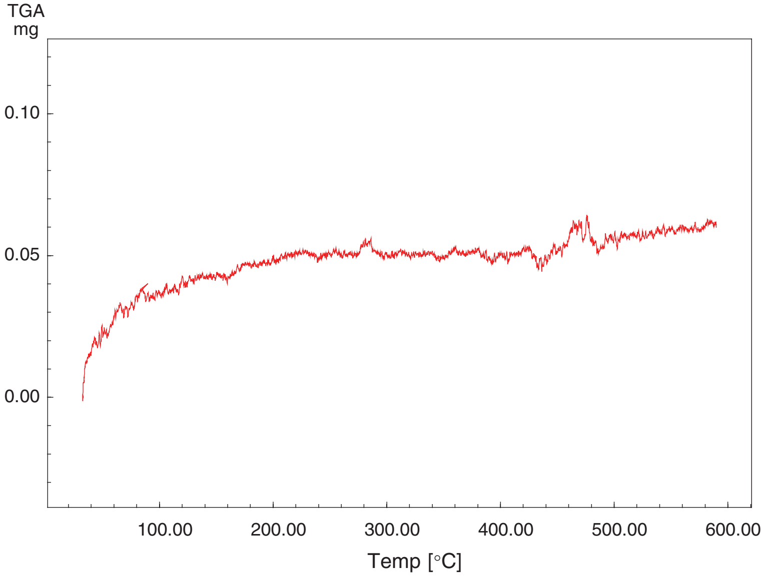

Fig. 8.3 The TGA graph of expanded graphite

in TGA. Firstly the increase in weight was due to the expansion of graphite, as graphite expands it trapped air inside and therefore its weight increase. Secondly as the atmosphere in which the sample was run cannot become a fully protective atmosphere (there will always be a little bit of air left inside argon atmosphere). As graphite is combustible it may combust to give carbon dioxide which can retain with graphite and increase its weight. Thirdly as the weight of the sample used in this run is very small (0.70 mg) because the sample is very light, there is a high uncertainty.

8.2.4 Synergist

The last type is known as synergist, and is of two types, one which is not a fire retardant but can work with other types of fire retardants to improve their fire retardancy. Antimony oxide is known as a synergist for halogenated alkanes. The second type (will be refer as synergist system) is where two or more fire retardants work together to improve overall fire retardancy of a material. Montmorillonite clay (MMT) is a fire retardant which works together with heat absorber and intumescent fire retardant [11–13]. Montmorillonite clay (MMT) can be used as a synergist for intumescent fire retardant and heat absorber [11, 12]. MMT has two opposing effects on the composite. One is barrier effect, MMT works by forming carbonaceous-silicate charred layer at the surface which protects the underlying material from heating up. The other is catalytic effect towards the degradation of polymer matrix which decreases thermal stability. Adding small amount ensures barrier effect but if too much is added then catalytic effect claim superiority [14]. Therefore only 5 wt% of MMT is added to the composite. Another synergism effect is between APP and EG. During heating APP decompose to give polyphosphoric acid, ammonia and water. Polyphosphoric acid assists the dehydration of EG to yield a carbonaceous residue which help protects material from further heating [9, 15].

8.3 Experimental Work Conducted by Other Researcher

8.3.1 Previous Work by Cai et al.

Cai et al. [1, 6, 9, 11, 12, 14, 15] begin their work on improving the fire-retardancy of paraffin (melting point between 54–56 °C) by preparing a form-stable PCM based on paraffin and HDPE (both with and without EVA) to provide structural integrity for paraffin. They also incorporated different types of fire-retardant into form-stable PCM and investigated their thermal stability and flammability properties as well. Various fire-retardant investigated including expandable graphite (EG), ammonium polyphosphate (APP), zinc borate (ZB), pentaerythritol (PER), brominated fire-retardant, melamine phosphate (MPP), antimony oxide (AO), melamine cyanurate (MCA), organophilic montmorillonite (OMT), magnesium hydroxide (MH) and red phosphorus microencapsulated with melamine formaldehyde (MRP). They also considered the synergist effect between some of these fire-retardant. All fire-retarded form-stable PCM were prepared by the twin screwed extruder. They have found that, for all of their work, TGA results suggested that even though the addition of fire-retardant promotes early onset temperature of degradation (due to decomposition of fire-retardant), the final results showed improvement in thermal stability of PCM due to the fact that there were approximately 5–20 wt% of residues at 800 °C (comparing to zero residue for form-stable PCM without fire-retardant). Additionally, DSC results confirmed that the addition of fire-retardant have little effect on the thermal storage properties of PCM.

Cai et al. [1] investigated the properties of fire-retarded form-stable PCM based on EG, EG + APP and EG + ZB. Cone calorimeter results suggested that there is a synergist effect between EG and APP as well as an anti-synergist effect between EG and ZB. The peak heat release rate (PHRR) for PCM containing EG was 108.7 kW/m^2 compared to 271.9 kW/m^2 for PCM containing EG + ZB and 85.8 kW/m^2 for PCM containing EG + APP. The synergist effect was attributed to the fact that APP is used as an acid source and decomposes into polyphosphoric acid with strong dehydration function during heating. The polyphosphoric acid participate in the dehydration of EG into carbonaceous and phosphocarbonaceous residue. These residues will act as a physical protective barrier. The gaseous substance resulted from the decomposition of APP causes the mixture of residues to swell, forming intumescent charred layer. The formation of charred residue and the swelling of the expanded graphite promote each other resulting into a better flammability property. However, in terms of ZB and EG, the anti-synergist effect was probably due to the formation of glassy film of B_2O_3 from ZB during heating. As a result, this material cover the surface of the material preventing EG from swelling into expanded graphite, which led to a worst flammability properties.

Cai et al. [6] investigated the flammability and thermal properties of fire-retarded form-stable PCM based on MPP + PER, brominated fire-retardant + AO and MCA. Cone calorimeter measurements have shown that, by comparing the PHRR between PCM with and without fire retardant, PCM containing brominated fire-retardant + AO had the best flammability property (62 % reduction of PHRR from PCM without fire-retardant) followed by PCM containing MPP + PER (56 % reduction) followed by PCM containing MCA (42 % reduction). Although brominated fire-retardant gave the best flammability results, it can cause severe contamination on the surrounding area. Therefore, it is more favourable to use MCA or intumescent fire-retardant like MPP + PER for improving flame retardancy of PCM.

Cai et al. [9] further investigated the flammability and thermal properties of fire-retarded form-stable PCM based on APP and APP + EG. Cone calorimeter results showed that the PHRR for PCM without fire-retardant is 884.2 kW/m^2 comparing to 532.6 kW/m^2 for PCM containing APP and 280.1 kW/m^2 for PCM containing APP + EG. It has been confirmed once again that the synergist effect existed between APP and EG even when a small amount (4 wt%) of EG was added. In addition to the synergist mechanism described earlier PO radical is produced from phosphoric acid during heating. PO radical can capture H and OH radical via gas phase flame retardant mechanism and further restrain the spread of fire.

Cai et al. [11] investigated the flammability and thermal properties of fire-retarded form-stable PCM based on MH, MH + MRP and MH + MRP + OMT. For this study, the supporting matrix is a mixture of HDPE and EVA in 3:1 ratio (instead of being 100 % HDPE). Cone calorimeter results showed that the PHRR for PCM without fire-retardant is 532.6 kW/m^2 comparing to 299.5 kW/m^2 for PCM containing MH and 176.2 kW/m^2 for PCM containing MH + MRP + OMT. It can be seen that there is a synergist effect between MH, MRP and OMT. The flame retarding mechanism of MH involve the decomposition reaction of MH into magnesium hydroxide (act as physical barrier) and water (act as heat sink). The addition of MRP produced a more compact residue due to the formation of different magnesium phosphate compound. As results, these compact residues are able to slow down heat and mass transfer between the gases and condensed phased and prevent the underlying polymeric substrate from further attack from the flame. Furthermore, MRP also possesses the ability to trap free radical in the gas phase which further improves the fire retardancy of PCM. The addition of OMT causes the residues to become more homogenous. As the amount of OMT increases, porosity on the surface of the residues decreases significantly. The compact and homogeneous residue increases the trapping of the decomposition products in the underlying material. As a result, the amount of flammable molecules and toxic combustion products are reduced, improving the fire retardancy of PCM.

Cai et al. [12] investigated the thermal properties of fire-retarded form-stable PCM based on APP + PER and APP + PER + OMT. For this study, the supporting matrix is also mixture of HDPE and EVA. Based on TGA results, PCM containing APP + PER + OMT is most thermally stable (highest residues at 800 °C) followed by PCM containing APP + PER followed by PCM without fire retardant. The addition of OMT increases the thermal stability of PCM due to the fact that OMT is more advantageous to form high-performance carbonaceous-silicate char layer on the surface which insulates the underlying material and slow the escape of the underlying products generated during thermal degradation.

Cai et al. [14] investigated the flammability and thermal properties of fire-retarded form-stable PCM based on OMT at different loading. For this study, the supporting matrix is also mixture of HDPE and EVA. Cone calorimeter results showed that the PHRR for PCM without fire-retardant is 1573.18 kW/m^2 comparing to 1378.30 kW/m^2 for PCM containing 2.5 wt% OMT, 1031.28 kW/m^2 for PCM containing 5 wt% OMT and 920.52 kW/m^2 for PCM containing 10 wt% OMT. Therefore, it can be clearly seen that fire-retardancy of PCM improved with increasing OMT loading. The addition of OMT resulted in a silicate layer during burning, which forms a protective barrier which limits oxygen diffusion to the substrate and slows the volatilization of the flammable decomposition product and thus protect the underlying material from further attack from fire. As OMT loading increases, the silicate layer becomes thicker and denser which further improve the protection of the underlying material from fire.

Cai et al. [15] investigated the properties of fire-retarded form-stable PCM based on MPP + PER and MPP + PER + OMT. Cone calorimeter measurements have shown that, by comparing the PHRR between PCM with and without fire retardant, PCM containing MPP + PER + OMT had the best flammability property (66 % reduction of PHRR from PCM without fire-retardant) followed by PCM containing MPP + PER (56 % reduction). The synergist effect was due to the reaction between MPP and OMT. This formed an aluminophosphate structure and a ceramic-like structure during burning. As a result, it acts as a protective layer preventing the underlying material from fire.

8.3.2 Previous Work by Zhang et al.

Zhang et al. [8, 16] conducted his research around improving the fire-retardancy of paraffin (melting point of 51 °C) by preparing a form-stable PCM based on paraffin and HDPE to provide structural integrity for paraffin. The main focus was on the intumescent fire retardant such as APP + PER + melamine (MA) and their synergist effect with EG and iron powder. Similar to Cai et al. works, all fire-retarded form-stable PCM were prepared by the twin screwed extruder. Additionally, DSC results were also similar to the results obtained by Cai et al.

Zhang et al. [8] investigated the properties of fire-retarded form-stable PCM based on (APP + PER + MA) and (APP + PER + MA) + EG. Cone calorimeter measurements have shown that, by comparing the PHRR between PCM with and without fire retardant, PCM containing (APP + PER + MA) + EG had the best flammability property (62 % reduction of PHRR from PCM without fire-retardant) followed by PCM containing APP + PER + MA (50 % reduction). The synergist effect between (APP + PER + MA) and EG was explained by the fact that EG improved the stability of the char layer (formed during heating by APP + PER + MA). As a result, the char layer can provide a more effective thermal protection property which led to better fire-retardant properties.

Zhang et al. [16] investigated the effect of iron powder on intumescent fire-retardant system (APP + PER + MA). Cone calorimeter measurements have shown that, by comparing the PHRR between PCM with and without fire retardant, PCM containing (APP + PER + MA) + 3 phr iron powder had the best flammability property (56 % reduction of PHRR from PCM without fire-retardant) followed by PCM containing (APP + PER + MA) + 5 phr iron powder (45 % reduction) followed by PCM containing (APP + PER + MA) + 10 phr iron powder (41 % reduction) followed by PCM containing (APP + PER + MA) + 1 phr iron powder (40 % reduction). The synergy between intumescent fire-retardant system and iron powder was attributed to the fact that the presence of iron powder stabilizes the intumescent char layer. As a result, fire retardant property of form-stable PCM improved. However, if too much iron powder is added, the negative effect may override the positive effect, due to the reduction in content on intumescent fire retardant system.

8.4 Experimental Work Performed at the University of Auckland

Paraffin (RT21), used in building application, poses higher flammable risk than those having higher melting temperature because of its higher vapour pressure. The work done at the University of Auckland was focused on how to reduce fire risk of a shape stabilized PCM with a low melting point such as paraffin RT21, which has not been investigated before. Different fire retardants are tested. The effect of best fire retardant was also tested on an ester based shape stabilized PCM, for the first time.

8.4.1 Tests for Fire Retardancy

8.4.1.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis can be used to describe the thermal stability of a material. In order for material to be thermally stable it must have two things: a high temperature of degradation and a large amount of residue [17]. Large residues also indicate that the material is resistant to fire which means that thermal stability is directly related to fire retardancy [1, 6, 12, 15]. Therefore TGA can be used to assess fire retardancy of material.

8.4.1.2 The Vertical Burning Test

Materials are to be burn vertically and the burning pattern can be classified into one of the Underwriters Laboratories (UL) 94 flammability rating as follow:

- 5VA (surface burn): Test specimens may not have a burn through (no hole). This is the highest (most flame retardant) UL 94 rating.
- 5VB (surface burn): Test specimens may have a burn through (a hole).
- V-0 (vertical burn): Burning stops within 10 s. No flaming drips are allowed.
- V-1 (vertical burn): Burning stops within 30 s. No flaming drips are allowed.
- V-2 (vertical burn): Burning stops within 30 s. Flaming drips are allowed.
- H–B (horizontal burn): Slow burning on a horizontal specimen burning rate. This is the lowest (least flame retardant) UL94 rating.

Dripping, whether or not cotton beneath catches fire, whether or not there is any sample/cotton residues left and whether or not material self-extinguish are all noted [13]. These are observable parameters which can be used to assess material reaction to fire. If cotton ignite when the sizes of drip is large and a lot of dripping occurs then material can spread flame quickly. Cotton residue determines how well dripping can cause burning. Small cotton residue means dripping cause burning well. Sample residue and whether or not sample can self-extinguish determines fire retardancy of sample. If residue is large or material can self-extinguish then material has high fire resistance. UL 94 rating cannot be given because this test is mainly used for plastic (samples prepared contained mostly PCM) and the burner is also not calibrated.

8.4.1.3 Cone Calorimeter

This test is considered to be the most important test which can be used to determine materials reaction to fire. This test involve placing a rectangular sample under a conical heater with a constant heat flux between 0 and 100 kW/m^2 and sample is ignited with an electrical spark igniter. Combustion products given off can be collect for further analysis. This test gives four aspects of material: ignitibility, combustibility, smoke production and production of toxic gas [8].

8.4.1.4 Differential Scanning Calorimeter (DSC)

DSC contained two sample holders inside; one is the reference and the other is for the sample. Heat is continuously supplied to both sample holders in order to determine the latent heat of the sample. The difference in temperature of both sample holders will give rise to a peak—indication phase change of material.

8.4.2 Materials for Fire Testing

Paraffin RT 21 is liquid at room temperature. In order to carry out fire testing experiment, samples will need to be a rectangular solid [8]. Therefore high density polyethylene (HDPE) is used as a supporting material since it has similar chemical structure as paraffin and a melting point well above room temperature [1, 6, 12, 15]. This allows a composite of paraffin/HDPE to retain solid form at room temperature. Additionally, fire retardants are also added during the mixing of HDPE and RT 21. Table 8.1 illustrated the composition of each samples.

8.4.3 Results and Discussion

8.4.3.1 Fire Retardancy and Fire Spread Using the Vertical Burning Test

The results in Table 8.2 clearly show that heat absorbers such as aluminium hydroxide and magnesium hydroxide had little effect in improving fire retardancy of the composite. Addition of heat absorber reduced dripping but a very small

Table 8.1 Samples identification and classification

Samples	Compositions
PCM1	60 wt% RT 20 + 40 wt% HDPE
PCM2	60 wt% RT 20 + 20 wt% HDPE + 20 wt% Magnesium Hydroxide
PCM3	60 wt% RT 20 + 15 wt% HDPE + 20 wt% Magnesium Hydroxide + 5 wt% MMT
PCM4	60 wt% RT 20 + 20 wt% HDPE + 20 wt% Aluminium Hydroxide
PCM5	60 wt% RT 20 + 15 wt% HDPE + 20 wt% Aluminium Hydroxide + 5 wt% MMT
PCM6	60 wt% RT 20 + 20 wt% HDPE + 20 wt% EG
PCM7	60 wt% RT 20 + 15 wt% HDPE + 20 wt% EG + 5 wt% MMT
PCM8	60 wt% RT 20 + 20 wt% HDPE + 20 wt% (APP + PER)
PCM9	60 wt% RT 20 + 15 wt% HDPE + 20 wt% (APP + PER) + 5 wt% MMT
PCM10	60 wt% RT 20 + 20 wt% HDPE + 10 wt% APP + 10 wt% EG

residue was obtained after burning. However when MMT was added together with heat absorber the size of residue increased, material self-extinguish and there was no dripping. This showed that there is a synergist effect between heat absorber and MMT which contributed to an improvement in fire retardancy of the samples. Cai et al. [11] used paraffin with melting temperature of 54–56 °C. Organophillic montmorillonite (OMT) was made by treating pristine montmorillonite by ion exchange reaction using hexadecyl trimethyl ammonium bromide (C16) in water. This treatment was done in order to increase the miscibility between clay and polymer matrix but the MMT used was treated differently. Cai et al. [12] used OMT together with microencapsulated red phosphorus (MRP) and magnesium hydroxide (heat absorber). They indicated that the results from both TGA and cone calorimeter have shown a significant improvement in thermal stability and fire retardancy of the samples, which suggested that there is a synergist effect between MRP, MH and OMT [12]. On the other hand intumescent fire retardant (IFR) showed a better improvement compared to heat absorber. Starting with EG (refer to PCM6 in Table 8.2), a small burning ashes were observed but distinguished quickly. This means that fire can spread quickly if ignition source is near, otherwise it may extinguish before it reaches an ignition source. The tested sample had a large residues and can self-extinguish indicating that it has high resistance to fire. The addition of MMT (refer to PCM7 in Table 8.2) did not have any significant effect. Using APP + PER (refer to PCM8 in Table 8.2) in intumescent system, significant dripping was observed but the material can self-extinguish. The material formed an insulating char layer protecting the underlying material from burning which results in medium size residues. An addition of MMT (refer to PCM9 in Table 8.2) to APP + PER system indicates a significant improvement in fire retardancy. The material had only few drips, sometimes none and it can also self-extinguish. There is a synergist effect between MMT and APP + PER which results in a formation of larger char layer, as reported by Cai et al. [12]. The addition of OMT together with IFR like melamine polyphosphate (MPP) + PER [15] and APP + PER [13] has increased fire retardancy of material by increasing the amount of residue [13, 15]. PCM10 (refer to Table 8.2) contained synergist system

Table 8.2 Vertical burning test results and comments

	Dripping	Cotton ignite	Cotton residue	Sample residue	Self extinguish	Comment	Fire retardancy
PCM1	Yes	Yes	None	None	No	A lot of dripping observed	Very poor
PCM2	Yes	Yes	Small	Very small	No	Three—four drips observed	Poor
PCM3	No	Yes	Medium	Small	Yes	Material broke apart due to decrease in mechanical property	Good
PCM4	Yes, during ignition	Yes	Small	Very small	No	Three—four drips observed	Poor
PCM5	No	Yes	Medium	Small	Yes	Material broke apart due to decrease in mechanical property	Good
PCM6	Small burning ash	Yes	Large	Large	Yes	Small ash drops often extinguish quickly	Good
PCM7	Small burning ash	Yes	Large	Large	Yes	Small ash drops often extinguish quickly	Good
PCM8	Yes, during ignition	Yes	Medium	Medium	Yes	A lot of dripping. Char formation	Good
PCM9	Yes/No[a]	Yes/No[a]	Large	Large	Yes	Few drips, sometimes none. Char formation	Very good
PCM10	No	Yes	Very large	Very large	Yes	Material broke apart due to decrease in mechanical property	Very good

[a] cotton did not ignite when sample did not drip

of APP + EG. The material does not drip, it can self-extinguish and it has a very large residues. This indicates that APP + EG system have higher fire resistance than normal intumescent system like EG only (PCM8). Cai et al. have tested EG by itself and have concluded that it was not as good as using EG with APP [9]. It was suggested that there is a synergist effect between EG and APP (refer to Sect. 8.2.4) resulting in an increased in residues and also a decreased in peak heat release rate which improved the overall fire retardancy of the material [8, 15].

8.4.3.2 Thermal Stability of Fire-Retarded Form-Stable PCM

Figure 8.4 shows the TGA analysis for the shape stabilized PCM containing no fire retardant. The figure shows three periods of mass loss. The first period is between 25 and 220 °C, the second period is between 220 and 510 °C and the last period is between 520 and 590 °C. It can be seen from Fig. 8.4 that nothing happens until the temperature reaches about 100 °C, where RT21 starts to decompose or evaporate until none remained at 220 °C (60 wt% loss). In the second period no mass loss is observed until the temperature reaches 450 °C where HDPE starts to decompose. The figure below shows that HDPE is fully decomposed at 520 °C leaving no residues.

Figure 8.5 shows that the addition of fire retardant to PCM produces similar TGA. It can be observed that up until 100 °C no mass loss occurs, and then the PCM starts to leave the sample until no PCM remained when the temperature reaches approximately 220 °C. It is only after that where the effect of fire retardant

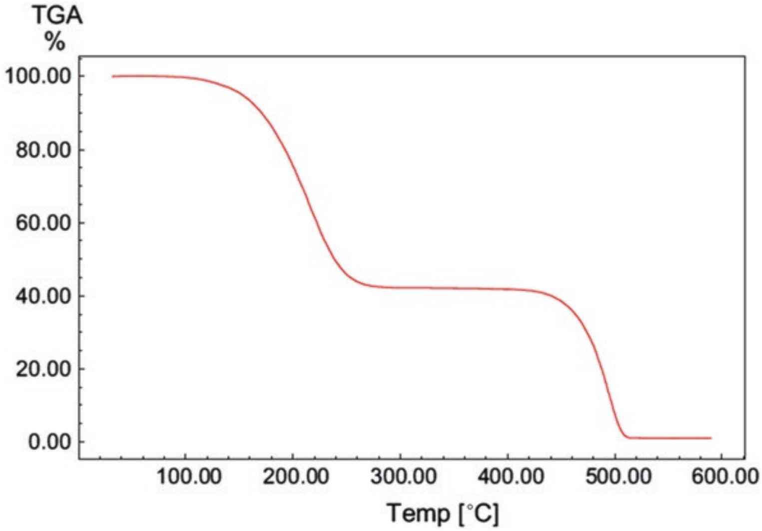

Fig. 8.4 TGA result showed that PCM1 degraded according to their constituent (RT21 and HDPE degraded at 120 and 450 °C respectively). There are no residues

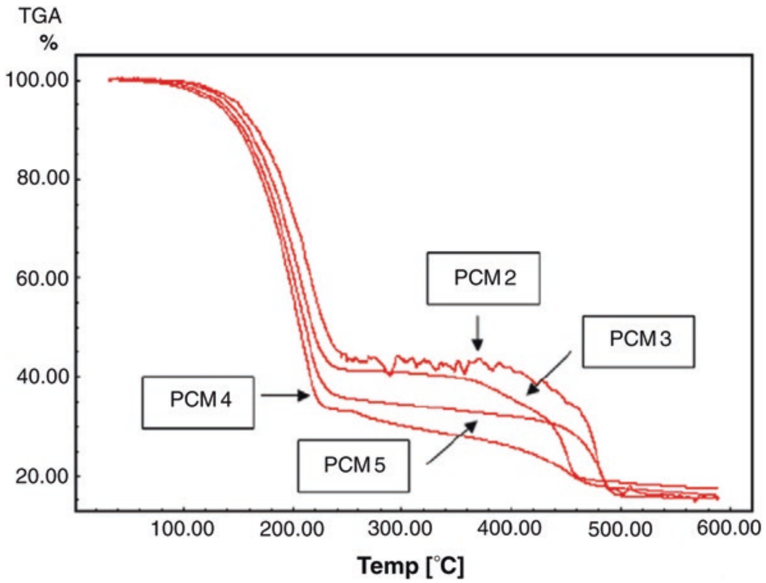

Fig. 8.5 TGA graph of form-stable PCM containing heat absorber (with or without MMT)

could be observed. At 220 °C the 60 % weight loss indicates complete loss of RT21 with no loss of HDPE while 70 % weight loss means 10 % of HDPE is also lost. With RT21, PCM2 (containing magnesium hydroxide) showed approximately 55 % weight loss while PCM4 (aluminium hydroxide) showed 67 % weight loss at 220 °C indicating magnesium hydroxide is a better fire retardant than aluminium hydroxide. The additions of fire retardants resulted in approximately 18 % residues at the end of the test, demonstrating that the material became more thermally stable.

Figure 8.5 also shows that an addition of MMT together with aluminium hydroxide (PCM5) slightly decreased the weight loss at 220 °C from 67 to 65 %. However, an opposite effect can be seen when MMT was added to magnesium hydroxide (PCM3). Adding MMT slightly increased the weight loss at 220 °C from 55 to 58 %. This suggested that MMT should only be used together with aluminium hydroxide.

It can be seen from Fig. 8.6 that the weight loss at 220 °C for PCM6, PCM7, PCM10, PCM8 and PCM9 were 48, 55, 59, 65 and 68 % respectively. The weight loss of PCM7 (contained EG and MMT) suggests that MMT should not be added together with EG as it increased the weight loss of PCM at 220 °C. PCM8 (10 % APP, 10 % PER) had higher weight loss than PCM10 (10 % APP, 10 % EG) indicating that the combination of APP + EG gives better fire retardancy. The weight loss of PCM9 suggests once again that MMT should not be used together with APP + PER. These results have shown that PCM6 had the best improvement in fire retardancy. However, as PCM6 had 10 % more EG than PCM8,

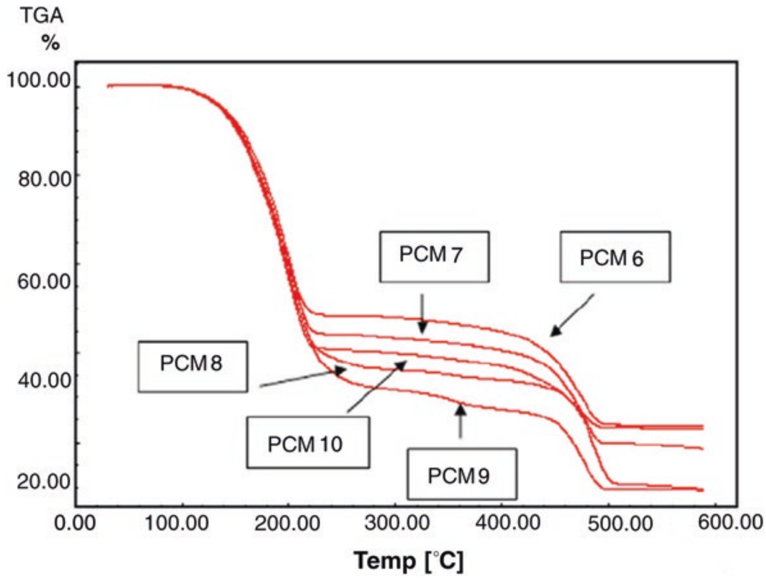

Fig. 8.6 TGA graph of form-stable PCM containing IFR (with and without MMT)

PCM9 and PCM10, accurate comparison cannot be made. Further investigation is necessary. The graph also shows that PCM6 and PCM7 (containing EG only and EG + MMT respectively) produced highest residues (high thermal stability) while PCM8 and PCM9 (containing APP + PER and APP + PER + MMT) produced smallest residues (low thermal stability). Addition of MMT did not show an improvement in thermal stability of the samples and it did not increase the amount of residue formed. PCM6 and PCM7 produced about 23 % residues; PCM10 produced 20 % residues while PCM8 and PCM9 produced only 10 % residues.

8.4.3.3 Flammability of Fire-Retarded Form-Stable PCM

Heat release rate, in particular peak heat release rate (PHRR), has been found to be the most important parameter in the evaluation of fire safety [11, 15]. Lower PHRR indicating that the material is more fire safe. Since the vertical burning test described in Table 8.2 shows that PCM10 has the best fire retardancy and due to the high cost of associated with the cone calorimeter test, the PHRR testing was conducted to PCM10 and PCM1 containing no fire retardant. It can be seen from Fig. 8.7 that PHRR of PCM1 and PCM10 (containing ammonium polyphosphate and expanded graphite) are 1,507 and 1,107 kW/m^2 respectively. Figure 8.7 shows that PCM1 contains two peaks, the reason for this could be the difference in the

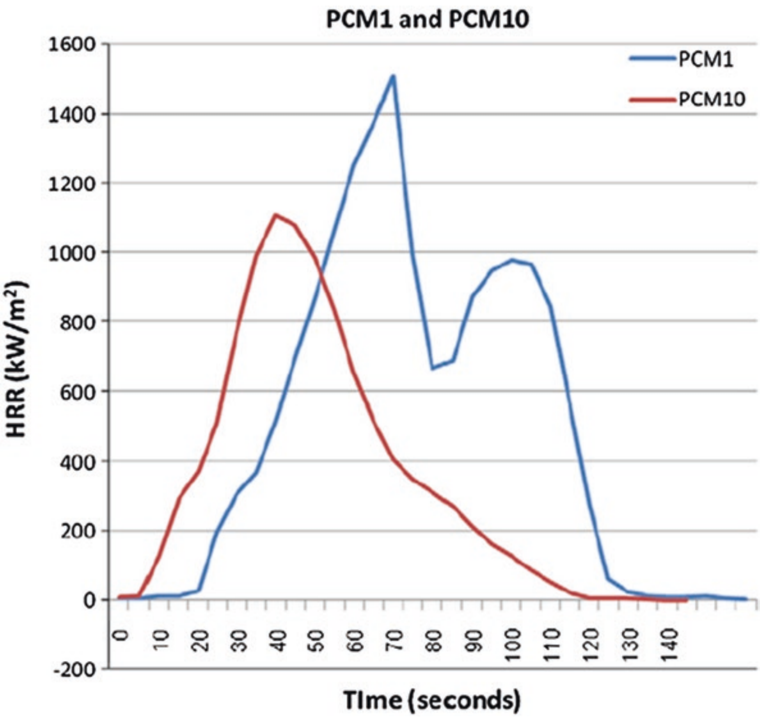

Fig. 8.7 Cone calorimeter of PCM1 and PCM10

heat of gasification of paraffin and HDPE, and the two peaks correspond to the flammability of the paraffin and HDPE, respectively [7].

It can be seen from Fig. 8.7 that PCM1 has two peaks while PCM10 only has one peak. The addition of EG and APP removed the second peak as well as reduced the peak HRR from approximately 1500–1100 kW/m^2 with the second peak became smoother.

This is due to the formation of char layer which protect the underlying material from further combustion. This clearly shows that an addition of fire retardant improved fire safety of PCM. Esters could also be used as PCM since they have good latent heat of melting within a suitable melting range. Figure 8.8 shows that heat flux generated from tallow propyl ester/HDPE composite (peak = 1100 kW/m^2) is lower than the corresponding one for paraffin (peak = 1500 kW/m^2) shown in Fig. 8.7, which is expected due to the lower vapour pressure of the ester. Figure 8.8 also shows how fire retardant could lower fire risk in the ester/HDPE sample (reduce the peak heat flux from 1100 to 800 kW/m^2). The fire retardant used was the same one used in PCM10. To our knowledge no one has tested fire hazard of shape stabilized PCM esters.

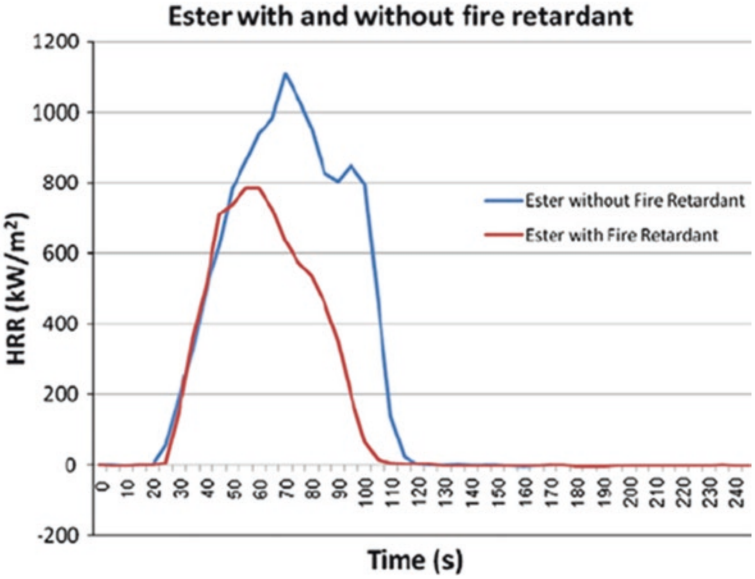

Fig. 8.8 Cone calorimeter of ester/HDPE with and without fire retardant

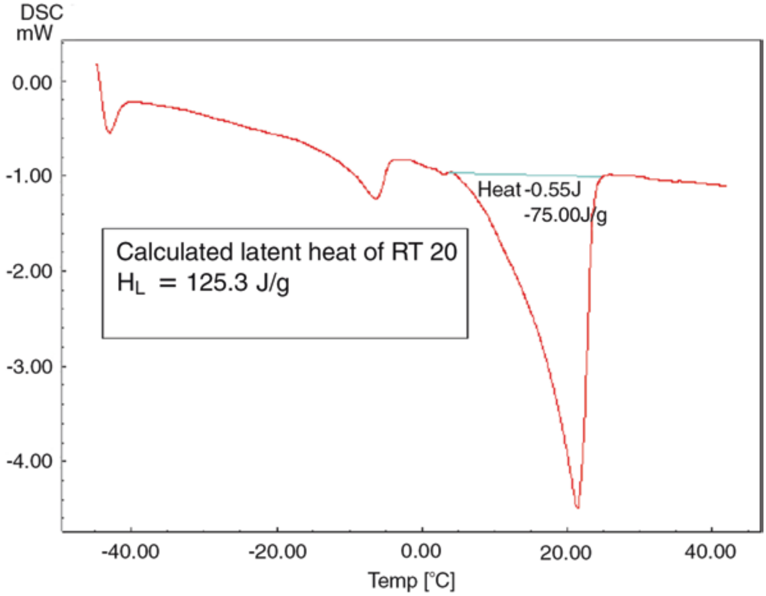

Fig. 8.9 DSC graph of form-stable PCM9

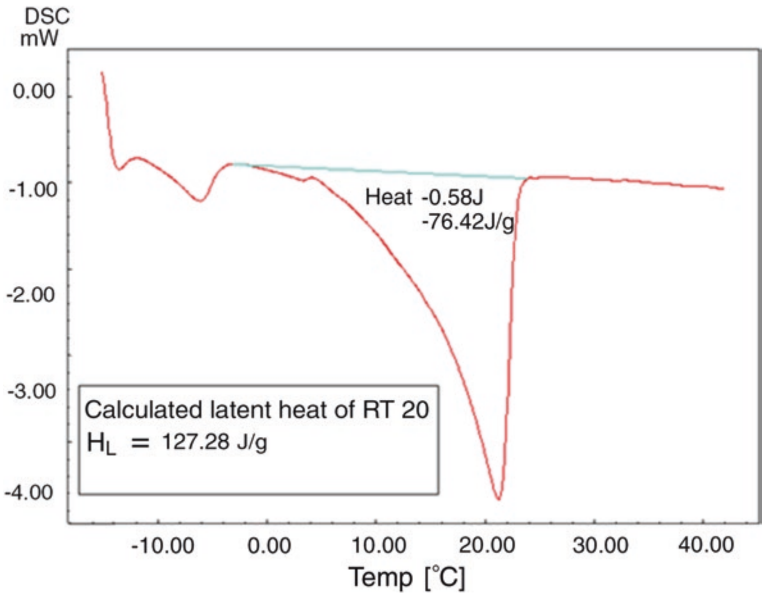

Fig. 8.10 DSC graph of form-stable PCM10

8.4.3.4 Latent Heat of Fire-Retarded Form-Stable PCM

The latent heat of RT21 is 136.3 J/g [16]. DSC tests were conducted to all samples but only two are presented since the addition of fire retardant show no effect other than the reduction in the latent heat due to the lower mass fraction of the PCM in the composites.

The DSC measurements shown in Figs. 8.9 and 8.10 are for RT21 in PCM9 and PCM10. When the measured latent heat is corrected based on the mass fraction of the PCM in the samples its value was reduced from 136.3 to 125.3 and 127.28 J/g respectively. This is very small reduction considering the common error involved in DSC measurements. Other samples behaved the same. Cai et al. [1] suggested that the molecular movement of paraffin with melting temperature of 54–56 °C was restricted by the three-dimensional network of form-stable PCM, therefore decreasing the latent heat. However, this difference is within the error associated with DSC measurements and hence a strong conclusion cannot be drawn.

8.5 Conclusions

Fire-retarded form-stable PCM was prepared using the Brabender Plastograph. The material used were based on RT21, HDPE and different fire retardants such as aluminium hydroxide, magnesium hydroxide, EG, APP, PER, MMT, IFR. Vertical burning test have shown that IFR is a better fire retardant for the PCM composite. Results indicated that PCM composite which contained IFR has better fire resistance than that containing heat absorber. TGA results showed that adding fire retardants to PCM composite has increased the amount of residues which contributed to an improvement in thermal stability. Cone calorimeter test indicated that an addition of fire retardant had improved fire safety of PCM by reducing peak HRR. DSC results have shown that an addition of fire retardant had little effect on the latent heat of PCM. It can be concluded that fire retardants used in PCM10 is the best. It showed a ‘‘very good'' rating from the vertical burning test (one of best two), 20 % residues (second best) from TGA and a clear reduction in peak HRR. Cone calorimeter tests carried out on shape stabilized tallow propyl ester showed lower heat peak indicating that esters are safer PCMs. Finally, it can be concluded that the incorporation of fire retardant into PCM reduced its flammability (as seen from the reduction of peak HRR). In an event of fire, as the combustion of PCM releases less heat, other building materials would combust less readily therefore this would increase evacuation time.

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Chapter 9
Flame Retardant Finishing for Textiles

G. Rosace, V. Migani, E. Guido and C. Colleoni

Abstract State of the art and perspectives on chemicals and techniques which have been developed in textile finishing for conferring flame retardant properties to natural and synthetic fibres are discussed in this review. An overview on the mechanism of combustion and fire retardancy is reported as well as the chemistry of flame retardants action, the different available types and their uses. The chemistry of molecules used to improve fire retardancy is discussed along with their thermal stabilities and flame-retardant properties. Simplified assumptions about the gas and condensed phase processes of flaming combustion provide relationships between the chemical structure of polymers and fire behaviour, which can be used to design fire-resistant textile materials. Moreover, an overview of currently accepted test methods on textile fabrics to quantify burning behaviour is reported. Finally, as a consequence of increasing commercial demands in terms of cost-effectiveness coupled with increasing concerns about the environmental and general toxicological character of flame retardant additives, some consideration is also given to both the novel approaches of the chemistry of antimony-free and halogen-free flame retardants and to attempts at increasing the efficiency of known chemistry to enhance char formation by intumescent action.

9.1 Introduction

A never greater requirement for superior, inexpensive and harmless materials has led to a fast propagation of high-performance equipments in building construction, automotive, electrical and electronics component, transport and textile industries. As protection is required in all these domains, the reduction in their flammability

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is a major concern. Particularly, according to statistics, about 50 % of fires are caused by textiles in the world [1]. Reaction to these alarms coupled with the request for enhanced flame retardant performance at a lower cost, has led both researchers and industry to increase the efficiency of presently used flame retardants, and to replace those where concerns lie with other existing formulations or to use known chemistry in novel ways. The use of flame retardants to reduce combustibility of the materials, and smoke or toxic gas production, therefore has become a fundamental part of the development and application of new materials. As a consequence, properties such as thermo-oxidative stability, low flammability and retention of material strength at elevated temperatures, low corrosion and better fatigue resistance, lower tooling costs, relative ease of fabrication and economical advantages are required [2]. In addition, the increasing pressure to replace toxic chemical combustion product materials have brought to a proliferation of antimony-, halogen- and formaldehyde-free fire resistant materials.

In this broad scenario, flame-retardant treatments, formulations, additives and finishes, mainly derived by the flame retardants chemistry developed in the 1950–1980 period, have been recently reviewed to provide textiles with important performance characteristics and to meet flammability requirements. Among the most important performance, the following are worth to be noted: little or no adverse effect on the physical properties of textile materials; retaining the aesthetics and physiological properties of textiles; produced by a simple process with conventional equipments and inexpensive chemicals; durable to repeated home launderings, tumble dryings and dry cleaning [3]. These textile requirements can satisfy the specific demand mainly in work clothing, firefighter apparel, draperies, institutional upholstery, institutional and commercial carpet, transportation, military garments, professional racers' garments and bedding. However, the development of flame retardant materials in household applications is also driven by environmental issues and many efforts are being made to identify and gather information on the type of flame retardants used in consumer products, to review and assess the toxicity and environmental impact of the currently used principal flame retardants.

9.2 Mechanism of Combustion

Combustion is an exothermic process which involves one or more reducing agents (combustibles) and an oxidizing agent (combustive, generally the oxygen in the air). Two requirements are necessary for the combustion process:

(1) a stoichiometric condition: the amount of combustible and oxidizer must be present in a suitable ratio;
(2) an energetic condition: the system must be supplied by enough energy to overcome the activation energy of the combustion process [4].

Polymers, due to their chemical structure made up mainly of carbon and hydrogen, are highly combustible. When exposed to a heat source, the temperature increases

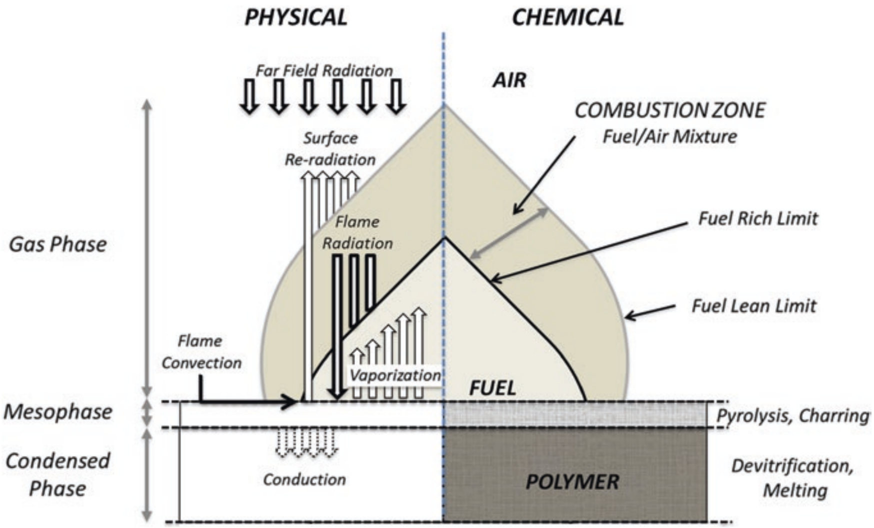


Fig. 9.1 Physical (*left*) and chemical (*right*) processes in polymer burning

and induces the polymer chemical bond scissions. Thermal energy from an external heat source (radiation, convection or conduction), chemical process induced inside the material (fermentation, oxidation, etc.) or exothermicity of the combustion reaction can be the cause of heating.

In general it can be stated that:

(a) macromolecules like polymers must be broken to generate a volatile combustible gaseous mixture, also called fuel. A continuous and large amount of thermal energy is necessary to sustain and maintain the combustion;
(b) gases and volatile liquids, with low molecular weight, form highly ignitable mixtures with air.

The fuel ignites when the auto-ignition temperature (defined as the temperature at which the activation energy of the combustion reaction is attained) is reached. Alternatively, the reaction with an external source of severe energy (spark, flame, etc.) can induce the fuel to ignite at lower temperatures (called the “flash point”).

The combustion process occurs in the following phases (Fig. 9.1):

- gas,
- mesophase (the interface between the gas and condensed phase during burning),
- condensed (liquid/solid).

Physical and chemical processes take place for each of them [5–7].

Physical processes include energy transport by radiation and convection between the gas phase (flame) and the mesophase and energy loss from the mesophase by mass transfer (vaporization of the pyrolysis gases) and conduction into the solid. The burning velocity of the flammable gases, when they are mixed with air, is much higher (about three order of magnitude) than the rate of release of the fuel gases from the gas-mesophase boundary. At the same time the polymer surface (mesophase) recedes with a rate that is still slower (about 10^{-3}m/s) than the previous one. As a result, the rate-limiting step in polymer flaming combustion is fuel generation, which is mainly directed by heat and mass transfer.

Chemical processes include:

- thermal degradation of the polymer in the mesophase as a consequence of the energy transport;
- mixing of volatile pyrolysis products with air by diffusion;
- combustion of the fuel-air mixture in a combustion zone (defined by a fuel-rich region on the inside and a fuel-lean region on the outside) that produces radiant energy over a spectrum of wavelengths including visible.

In cases where the heat supplied from the ignition source is exhausted or negligible when compared to that transmitted to the polymer in the combustion cycle, the process becomes a self-sustaining one. The temperature requirements needed to support it are in fact satisfied by the heat carried by the thermoxidation reactions that occur in the gas phase (in the flame) or in the condensed phase (in the material). The extension of the flame is related to the heat of combustion of the polymer: the higher the heat, the greater the amount of heat released by the flame to sustain the combustion cycle.

The whole combustion process is then the result off our steps of reactions:

(1) heating;
(2) decomposition;
(3) ignition;
(4) combustion and propagation.

During the heating phase an external ignition source raises the material temperature at a level that depends on the intensity of the thermal ignition source and on the thermal properties of the material (such as thermal conductivity, specific heat, latent heat of fusion and vaporization). The material temperature raises until it reaches its decomposition temperature, which varies–depending on the polymers-from 180 to 500 °C and above.

The decomposition mechanism is highly dependent on the weakest bonds, and can occur in both oxidizing and non-oxidizing conditions.

Non-oxidizing thermal degradation starts by chain splitting due to the effect of temperature (pyrolysis). It depends on the presence of chain and catalyst residues with oxygen atoms, former residues of oxidation, polymer chains with chemical defects and weak bonds along the chain. Chain cracking can occur in two ways:

- by formation of free-radicals ($R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 = R_1\text{-}CH_2^{\bullet} + {}^{\bullet}CH_2\text{-}R_2$) that start a chain-reaction under both oxidizing and non-oxidizing conditions.
- by migration of hydrogen atoms and the creation of an alkene ($R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2 \rightarrow R_1\text{-}CH = CH_2 + CH_3\text{-}R_2$).

Low molecular weight products like carboxylic acids, alcohols, ketones, aldehydes, and reactive species, like $H^{\bullet}$ and $HO^{\bullet}$ are produced in oxidizing thermal conditions by reaction of the polymer with the oxygen in the air. Recombination reactions by crosslinking of the macromolecular radicals are then induced by the initial oxidation, although bond scission normally remains the main reaction. The wrenching reaction of hydrogen atoms from the polymer chains [4] controls the propagation rate of the degradation process.

Polymers like other fuels produce, upon pyrolysis, species capable of reacting with air oxygen and producing the reaction scheme (Eqs. 9.1 and 9.2), which propagates the fuel combustion by the branching reactions [8].

$$H^{\bullet} + O_2 \rightleftarrows HO^{\bullet} + O^{\bullet} \tag{9.1}$$

$$O^{\bullet} + H_2 \rightleftarrows HO^{\bullet} + H^{\bullet} \tag{9.2}$$

The main exothermic reaction in the flame is expressed by (Eq. 9.3):

$$HO^{\bullet} + CO \rightleftarrows CO_2 + H^{\bullet} \tag{9.3}$$

which provides most of the energy maintaining the combustion. Chain branching reactions (9.1) and (9.2) must be hindered to delay or to stop the combustion process.

As the reaction continues, a chain propagation mechanism forms more and more radicals but, while the initiation step is necessarily endothermic, subsequent stabilization and propagation are over all exothermic with radicals $H^{\bullet}$ and $^{\bullet}OH$ giving rise to exothermic reactions [9]. In many cases, a solid carbon aqueous residue is also produced, which delays the contact between the air and the gaseous products of decomposition and slows the transmission of heat to the polymer.

Then, depending on the intensity of external heat, on the temperature required for decomposition and on the rate of decomposition, gaseous combustion products are finally formed. The concentration of flammable gases increases until it reaches a level that allows sustained oxidation in the presence of the ignition source. The combustion of the gases increases the polymer temperature and thus supports the pyrolysis and production of new combustible gases. Combustion thus continues even in the absence of an external heat source. The ability to self-support mainly depends on the exit speed of the pyrolysis gas from the surface, which accelerate the decomposition phenomena. The whole polymer combustion process is summarized by Fig. 9.2.

Generally speaking (Scheme 9.1), energy is:

- required (endothermic phase) for:
  - i. heating the fibre to the pyrolysis temperature (melting processes with thermoplastic fibres),
  - ii. the pyrolysis reaction,
  - iii. evaporation of the pyrolysis products,
  - iv. heating the breakdown products to the ignition temperature,
  - v. compensation for the heat lost to the surroundings;
- produced (exothermic phase) by:
  - i. exothermic reaction of the breakdown products.

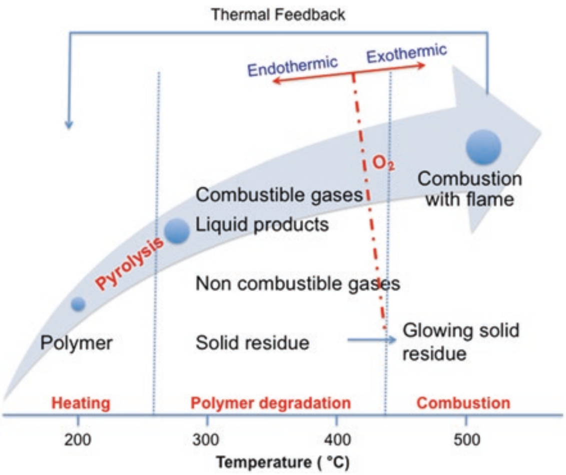
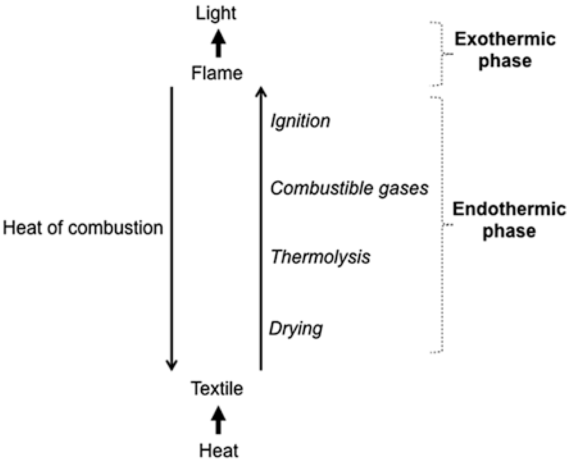


Fig. 9.2 Schematic representation of polymer combustion process



Scheme 9.1 Schematic diagram of the thermal energy, absorbed or emitted, during combustion of textiles

When textile material is burned, depending on its organic nature, CO, CO_2 and other gases as HCN, HCl, H_2S, SO_2, NO_2 and numerous compounds (such as acrolein, acetaldehyde, isocyanates etc.) can be formed. The most important products of pyrolysis and combustion (combustion gases) of the main textile fibres are reported in Table 9.1.

A particular type of combustion that occurs without the generation of flames is smoldering, or glowing, combustion. It is a slow, low-temperature, flameless form of combustion, sustained by the heat evolved when oxygen directly attacks the surface of a condensed-phase fuel. Smoldering constitutes a serious fire hazard because it typically produces a higher conversion of a fuel to dangerous burning compounds. Moreover, it also provides a pathway for the flame that can be

Table 9.1 The most important products of pyrolysis and combustion (combustion gases) of various textile fibres [10]

Fibre		Products of pyrolysis and combustion
Natural	Cellulose	CO, CO_2, H_2O, methanol, ethanol, furane derivatives, formic acid, acetic acid, formaldehyde, acetaldehyde, acrolein, hydrocarbons
	Wool	CO, CO_2, H_2O, H_2S, SO_2, ammonia, amines, HCN, H_2, lower hydrocarbons (CH_4)
Man made	Aramids	CO, CO_2, H_2O, saturated and unsaturated lower hydrocarbons, acetaldehyde, acetone, HCN, NH_3, benzene, benzonitrile, acetonitrile, NO_2, toluene, acetic acid
	Cellulose acetate	CO, CO_2, H_2O, acetic acid, methane, ethylene etc., hydrocarbons up to C6, furane, vinyl ether, methanol, acetone, acetaldehyde, acrolein, ethyl acetate, benzene
	Polyacrylonitrile	CO, CO_2, H_2O, CH_4, ammonia, nitriles, HCN, acrylonitrile, lower hydrocarbons
	Polyamides	CO, CO_2, H_2O, mono and dicarboxylic acids, adipic acid, cyclopentanone, hydrocarbons, ammonia, amines, HCN, acetaldehyde, formaldehyde, caprolactam, benzene
	Polyester	CO, CO_2, H_2O, acetaldehyde, benzoic acid, terephthalic acid, acetic acid, hydrocarbons, CH_4, benzene, vinyl benzoate, divinyl terephthalate
	Polypropylene	CO, CO_2, H_2O, saturated and unsaturated hydrocarbons, propylene, pentene, ketones, acetone, aldehydes, formaldehyde, acrolein, methanol, formic acid, acetic acid

initiated by heat sources too much weak to produce a flame. Nevertheless, when a non-flaming response of condensed-phase organic materials to an external heat flux is observed, sometimes the term smoldering is inappropriately used to describe no oxidation process. This process must be more appropriately attributed to a forced pyrolysis, and not to smoldering.

The physical factors that favor smoldering are mainly caused to the large surface area (per unit of mass) of the finely-divided particles of combustible that facilitates surface attack by oxygen. At the same time, oxygen transport to the reaction site by diffusion and convection is also favoured by the permeable nature of the aggregate particles.

Moreover, physical factors have to be complemented by chemical factors as well. For example all cellulosic materials, when degraded thermally, form a char, a material richer in carbon than the original fuel with an enhanced surface area per unit mass. A char has a great heat of oxidation and it can be rapidly attacked by oxygen at moderate temperatures ($\geq$400 °C) to form mainly CO and CO_2 [11]. The oxidation process is facilitated not only by the enhanced surface area but also by alkali metal impurities which act as catalysts. So, char oxidation is the principal heat source in most self-sustained smolder propagation processes and consequently, any material that produces a significant amount of char during thermal decomposition can be susceptible to smoldering combustion.

Finally, a specific classification for textile materials distinguishes organic molecules of textile fibers as melting or non-melting: in the first case (mainly for synthetic fibers) melting, evaporation and combustion reactions occur. In the second case (for natural or artificial fibers) the heated material doesn't melt, but the breaking of a number of covalent bonds, with subsequent destruction of the structure and the formation of volatile products and carbonaceous residues occur. Combustion reactions mostly take place in the gas phase, even if the fuel is liquid or solid, because of evaporation or decomposition reactions with production of highly flammable gases.

A number of thermal transition temperatures and thermodynamic parameters influences the burning behavior of fibers. Four thermal transitions are known for fibers, in addition to their typical values of flame temperature and heats of combustion: the physical glass (T_g) and melting (T_m) transitions, the pyrolysis temperature (T_p) and the onset of flaming combustion (T_c) [6]. Generally, for natural cellulosic fibers and for some synthetic fibers like the acrylics, the lower the T_c temperature (and usually T_p), the hotter the flame, the more flammable is the fiber [12].

In conclusion, a schematic overview of the fire behaviour of textile materials can be drawn. Natural fibers, such as cotton and linen, are amongst the most flammable textiles and they burn with hot flames and light smoke. They can also continue to smolder, causing fires to re-ignite or propagate. Rayon burns vigorously like cotton, but it may shrink. On the contrary, wool and leather burn slowly and are difficult to ignite if compared to synthetics (such as acrylics, polyesters, polyolefins or polyamides), which burn rapidly and drip considerably. Finally, some other synthetics burn unlikely (i.e.: Aramid) due to their intrinsic fire-retardant properties.

9.3 Mechanism of Flame Retardancy

A completely non-combustible organic material that retains the characteristics of ease of fabrication, low specific weight and cost is not achievable. The use off lame retardants is however suitable to decrease the ease of ignition and/or the speed of propagation of the combustion of the polymers.

A fire-retardant product must contrast the combustion process and, possibly, stop it by using multiple synergistic mechanisms, realized in:

(a) **condensed phase**, on the substrate, to affect its pyrolysis, the development of non-combustible gases and the formation of intumescent which reduce the contact with the oxygen;
(b) **gas phase**, on the volatile fuels products and their interaction with oxygen, by introducing inhibiting factors (free radicals).

The most common system in order to reduce the danger of burning is to use flame retardants acting by physical and chemical actions, which are divided into:

(1) Physical action	(1.1) Formation of a protective layer (coating): the material is protected with a solid or gaseous protective layer and protected from heat and oxygen necessary for the combustion process
	(1.2) Dilution: inert substances and additives evolving noncombustible gases dilute the fuel in the solid and gaseous phases
	(1.3) Cooling: energy absorbing (endothermic) processes triggered by additives and the chemical release of water cool the substrate of material to a temperature below that required for sustaining the combustion process
(2) Chemical action	(2.1) Reaction in the solid phase: the flame retardant builds up a char layer and shields the materials against oxygen. It provides a barrier against the heat source creating a carbonaceous surface structure by cyclization and crosslinking of double bonds
	(2.2) Reaction in the gas phase: the radical gas phase combustion process is interrupted by flame retardant, resulting in cooling of the system, reducing and eventually suppressing the supply of flammable gases

All the above listed products may be added to the substrate sorchemically bound to the macromolecules and they can be classified in two categories:

(1) Additive flame retardant	They are usually mineral fillers, hybrids or organic compounds and they are generally incorporated into/deposited onto polymeric fibers by physical means
(2) Reactive flame retardants	They involve either the modification of existing polymers through copolymerization or the post-reaction process (e.g. chemical grafting or coating) with flame retardant chemicals

Table 9.2 Classification of flame retardants as function of their durability on textiles

Classification of flame retardants	Treatment characteristic	Some example of additives, depending on the treated textile
Durable	It imparts flame-retardant properties to textiles and textile products durable for many washing cycles (e.g. 50 launderings)	• Dimethyl (N-hydroxymethylcarbamoylethyl) phosphonate • Tetrakis-(hydroxymethyl)phosphonium chloride
Semi-durable	It resists very few launderings	• Salts of polyethylene with aminoalkylphosponic acids • Modified guanidine phosphate • Insoluble salts of amphoteric cations or anions
Non-durable	It is generally water-soluble inorganic salt that is easily removed by water, rain, or perspiration	• Boron derivatives, boric acid, and borax, sometimes in conjunction with ammonium salts of sulfuric and phosphoric acid, urea, and ammonium bromide • Inorganic acids, acidic salts, and salts capable of releasing an acid upon its ammonium salt

Finally, according to the specific durability effects on the textile substrates, flame retardants could be classified in non-durable, semi-durable and durable, with respect to a given condition. Durability refers to the ability of a flame-retardant textile to withstand washing/cleaning, chlorine bleaching, weathering and sun exposure. The definition of durability must be related to the conditions of use of the textile and the product as reported in Table 9.2 [13].

9.4 Chemistry of Flame Retardant Additives

There are three main families of flame-retardant chemicals [4]:

a. Inorganic flame retardants;
b. Halogenated flame retardants;
c. Phosphorus-based flame retardants.

Nitrogen or Phosphorus-Nitrogen based flame retardants and intumescent systems are also employed.

9.4.1 Inorganic Flame Retardants

Inorganic compounds are suitable for use as flame retardants in textiles, due to their decomposition temperatures in the range 150–400 °C. Unlike organic compounds, inorganic flame retardants do not evaporate under the influence of heat; rather they decompose, giving off non-flammable gases like water, carbon dioxide, sulphur dioxide, hydrogen chloride, mostly in endothermic reactions. Due to their properties to reduce the content of combustible products and to modify the thermal conductibility of the material, they are used alone or in combination with other flame retardants to obtain the required fire retardant properties. The most commonly used inorganic flame retardants are aluminium or magnesium hydroxides and their action is correlated with temperature rise: they can be decomposed endothermically and release non-flammable molecules (H_2O and CO_2), able to dilute flammable gases and to promote the formation of insulator layer.

Aluminium trihydroxide ($Al(OH)_3$) is the most widely used flameretardant. It is an inert mineral filler, a non-toxic, white, crystalline powder and is included in the inorganic flame retardants. At about 250 °C, this compound is decomposed to form aluminium oxide and water, thus obtaining a non-flammable protection on the surface of the treated material, according to (Eq. 9.4):

$$2\mathrm{Al(OH)_3} \xrightarrow{\Delta} \mathrm{Al_2O_3} + 3\mathrm{H_2O}\ (-298\,\mathrm{kJ/mol}) \tag{9.4}$$

The endothermic reaction slows down combustion and cools the treated material. The product is low cost and non-toxic, but strong percentages of $Al(OH)_3$ are required to achieve effective retarding action.

Antimony trioxide (Sb_2O_3) the compound doesn't show intrinsic flame retardant properties, but it has an effective synergistic effect in combination with halogenated flame retardants because it acts as a catalyst, and it helps the decomposition of halogenated flame retardants to form active molecules which remove the radicals involved in the propagation of the flame [2]. It reacts with hydracids generated by the halogenated flame retardants to form antimony oxyhalides that lead to the formation of $SbCl_3$ or $SbBr_3$, which act as scavengers of radicals, such as $H^\bullet$ (Eqs. 9.5–9.7).

$$SbCl_3 + H^\bullet \quad \rightarrow \quad HCl + SbCl_2{}^\bullet \tag{9.5}$$

$$SbCl_2 + H^\bullet \quad \rightarrow \quad HCl + SbCl^\bullet \tag{9.6}$$

$$SbCl + H^\bullet \quad \rightarrow \quad HCl + Sb^\bullet \tag{9.7}$$

The scavenging of radicals is further obtained by antimony oxide and $Sb^\bullet$ as reported in (Eqs. 9.8–9.10):

$$Sb^\bullet + HO^\bullet \quad \rightarrow \quad SbOH \tag{9.8}$$

$$SbOH^\bullet + H^\bullet \quad \rightarrow \quad SbO^\bullet + H_2 \tag{9.9}$$

$$SbO^\bullet + H^\bullet \rightarrow \quad SbOH \tag{9.10}$$

Magnesium hydroxide ($Mg(OH)_2$) its action mechanism is similar to the aluminium trioxide's but is decomposed at relatively high temperatures (more than 300 °C), according to (Eq. 9.11):

$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O\ (-200\ \mathrm{kJ/mol}) \tag{9.11}$$

Boron derivatives they act by releasing water, in an endothermic reaction, and by forming an insulating layer on the surface of the treated material. As the temperature increases the molecules lose water and form a glassy coating to protect textiles (Eq. 9.12):

$$2H_3BO_3 \quad \xrightarrow[-2H_2O]{130-200\ ^\circ C} \quad 2HBO_2 \xrightarrow[-H_2O]{260-270\ ^\circ C} B_2O_3 \tag{9.12}$$

This process takes place at temperatures below the fiber pyrolysis temperature. Zinc borate ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$) is a multifunctional flame retardant which can function as a flame retardant to reduce emissions of smoke [14], to promote carbonization and to create a synergy to increase the effectiveness of halogenated and nitrogenated flame retardants [15].

Phosphorus compounds

Elemental red phosphorus acts in small quantities (less than 10 %) as a flame retardant by its oxidation to phosphoric acid or phosphoric anhydride during the combustion process. These products can catalyze the dehydration reaction of polymer end chains and trigger char formation. It is commercially used for polyamide 6 and 6.6, but also suitable for other polymers.

Ammonium polyphosphate is an inorganic salt of polyphosphoric acid and ammonia. Its thermal degradation creates polyphosphoric acid able to react with the oxygen- or nitrogen-containing polymers catalyzing their dehydration reaction and char formation.

It is used for intumescent systems in coatings and its performances depend on the applied amount.

9.4.2 Halogenated Flame Retardants

The properties of these compounds strongly depend from the type of halogen used. They can be divided into aromatic, aliphatic and cycloaliphatic products and they act by effectively removing radicals thus reducing heat generation and so the production of further gaseous flammable materials. Halogen containing flame retardants, when exposed to high temperatures, react in the gas phase with hydrocarbon molecules (flammable gases) by free-radical inhibition to give HX. High-energy $HO^\bullet$ and $H^\bullet$ radicals formed during combustion are removed by halogen released from the flame retardant (MX) (Eq. 9.13):

$$MX \rightleftarrows X^\bullet + M^\bullet \tag{9.13}$$

The halogen radical $X^\bullet$ reacts with the fuel RH producing hydrogen halide HX (Eq. 9.14):

$$RH + X^\bullet \rightleftarrows R^\bullet + HX \tag{9.14}$$

The halogen halide HX is believed to be the actual flame inhibitor by inhibiting the fuel chain propagation (Eqs. 9.15–9.16):

$$HX + H^\bullet \rightleftarrows X^\bullet + H_2 \tag{9.15}$$

$$HX + HO^\bullet \rightleftarrows X^\bullet + H_2O \tag{9.16}$$

The $X^\bullet$ radical formed is less reactive, effectively reducing the heat available for perpetuating the combustion cycle. The effectiveness of halogen-containing flame-retardants decreases in the order I > Br > Cl > F.

Fluorine and iodine-based compounds are not used because they do not release halogen radicals at temperature close to the polymer decomposition (the bond between fluorine and carbon is too strong) or they are not enough thermally stable (Iodine-based compounds).

Consequently, bromine and chlorine compounds are the only halogen compounds having commercial significance as flame-retardant chemicals. With respect to processability, halogenated flame retardants vary in their thermal stability [16].

However, the potential risk of environmental impact of those products, particularly of polychlorinated biphenyls (PCBs), has required its replacement with polybromine diphenyl ethers (PBDE), in which the presence of oxygen between the two phenyl rings makes them biodegradable and non-toxic. In particular, the decabromodiphenyl ether has become one of the most effective flame retardant actually used. However, recent researches have shown that, as a result of pyrolysis and thermoxidation, the polybromine diphenyl ethers may give rise to polybrominedibenzodioxins (PBDD) and polybrominedibenzofurans (PBDF) whose toxicity is comparable with that of the corresponding chlorinated compounds.

9.4.3 Phosphorus-Based Flame Retardants

Phosphorus-based chemicals are one of the main classes of flame retardant used for polymers, in plastics and textiles. They can be classified in:

- organic molecules (generally alkyl and aryl phosphates, phosphonates, etc.);
- inorganic compounds, like red phosphorus and ammonium polyphosphate.

Phosphorus-based flame retardants act both in gas and in condensed phase. In the gas phase, the phosphorus compounds can form active radicals, like $PO_2^\bullet$, $PO^\bullet$ and $HPO^\bullet$ which are able to act as scavengers of $H^\bullet$ and $HO^\bullet$ radicals. In the mean time, the water released by the condensation of phosphoric acid dilutes the oxidizing gas phase. The efficiency of the process is higher than the one of the bromine derivatives, but the amounts of add-on required are detrimental for the whole application.

In the condensed phase, the thermal decomposition of phosphorus-containing flame retardants turns into phosphoric acid, which is able to link hydroxyl group of polymers, and leads to the formation of carbocations and carbon-carbon double bonds. The obtained char inhibits the pyrolysis process which is necessary to feed flames. It protects the polymer from the combustion, thus decreasing (a) the amount of volatile products, (b) the heat generated by the flame (c) the oxygen diffusion.

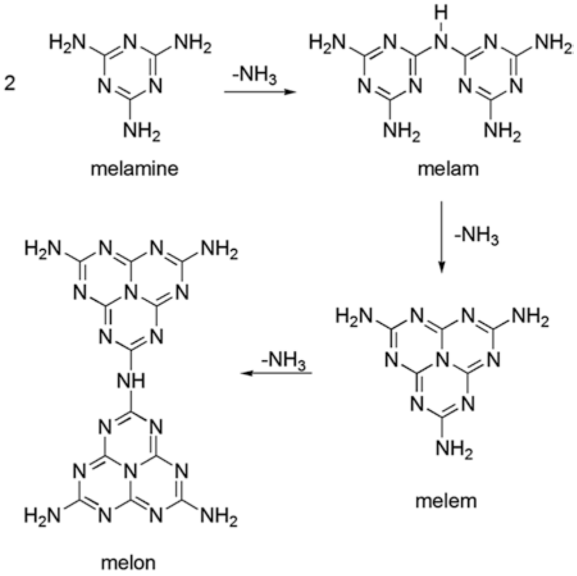
9.4.4 Nitrogen-Based Flame Retardants

The melamine–based are the currently most used products and they can can be distinguished: pure melamine, melamine derivatives (i.e. salts with organic or inorganic acids such as boric acid, cyanuric acid, phosphoric acid or pyro/polyphosphoric acid) and melamine homologues such as melam, melem and melon. Their action is due to the endothermic decomposition that undergoes when this is subjected to heating (250–400 °C). Decomposition produces ammonia and forms cyclic compounds called melem, melam or melon, which constitute the surface layer of char, as reported in Fig. 9.3:

The action of nitrogen-containing flame retardants is carried out through several mechanisms:

- In the condensed phase, melamine is transformed into cross-linked structures which promote char formation. These are relatively stable at high temperatures and physically inhibit the decomposition of materials in flammable gas;

Fig. 9.3 Decomposition scheme of melamine-based products by heating (250–400 °C)



- in the gas phase the nitrogen obtained by ammonia released at the pyrolysis temperature, dilute oxidizing and flammable gases;
- in conjunction with phosphorus, the nitrogen appears to enhance the attachment of the phosphorus to the polymer.

9.4.5 Synergistic and Additive Effects in the Flame Retardancy

Synergistic trends, based on chemical and physical interactions between the basic flame retardants agents and one or more chemicals, have been observed in many systems based on all above mechanisms. Although numerous studies referring to the P-N synergism for cotton have been published so far, to the best of our knowledge, only a qualitative observation of this phenomenon has been argued. Lewin [17] and Horrocks [18] have demonstrated that it is possible to identify a real synergism between two species (namely, phosphorus and nitrogen) only through the calculation of a synergism effectiveness parameter. Indeed, in some cases, the effect of the two species can be merely additive or even antagonist [19].

Although some chemicals have only small flame retarding effects by themselves, they are able to increase the flame retardancy of primary flame retardants (nitrogen with phosphorous and antimony with halogens). For example, the synergistic combination of phosphorus-nitrogen flame retardants is suitable for cellulosic fibers and it generates primary active compounds like H_3PO_4 and P-amides.

Moreover, methylolmelamine have some flame retardant activity in their own right and incorporation of amino structures in carbohydrates is reported to favor decomposition at lower temperatures to water plus char [20]. Combinations of nitrogen compounds such as urea or methylolmelamine with acids such as phosphoric acid produce, upon exposure to flame, intumescent chars which tend to protect the underlying combustible substrate, because of their good thermal insulating character. Elemental analyses of char residues show that effective N-P combinations leave a P-N-O-thermally stable amorphous substance, in the residue [21, 22]. Nitrogen acids could also form an acid char and nitrogen oxides may act as flame free-radical traps in the vapor phase. In fact, organo phosphorus flame retardants that contain synergistically active nitrogen could show higher effectiveness as compared with pure phosphorus counterparts. In P-N synergistic retardants, the amine nitrogen acts as a nucleophile, attacking the phosphate and creating polymeric species having P-N bonds. These latter are more polar than the already present P-O bonds, and the enhanced electrophilicity of the phosphorus atom increases its ability to phosphorylate the C(6) primary hydroxyl group of cellulose. By this way, the intramolecular C(6)–C(1) rearrangement reaction forming levoglucosan is blocked. Meanwhile, the auto-crosslinking of cellulose promotes and consolidates the char formation derived by the action of the same flame retardants. The effectiveness of the halogen containing retardants is strongly enhanced by the synergy with antimony compounds, probably due to the formation of antimony halides (e.g. $SbBr_3$) which are heavier and more stable than their respective derivation acids (such as HBr), thus intercepting the free radicals and shielding from oxygen for a longer time. A similar synergistic effect is observed between the halogenated flame retardants and some phosphorus compounds. The halogen-Sb_2O_3 combination is especially suitable for synthetic fibres and it produces SbOX and SbX_3 compounds. Synthetic fibres could be also finished by phosphorus-halogen combinations, and their main reaction products are basically POX_3 and PX_3 compounds. The synergistic effect of antimony comes from the volatility of antimony trihalides and the effectiveness of antimony compounds in scavenging free radicals over a broad temperature range.

Zinc borate is a synergist of chlorine and bromine containing flame retardants or polymers. Its efficacy depends on the type of halogen source (aliphatic vs. aromatic) and the base polymer used. The zinc borate can generally display synergistic effects with antimony oxide in fire retardancy. This synergy can be more remarkable when used in conjunction with aluminium trihydrate or magnesium hydroxide.

Recently [19], the effect of three potentially synergistic agents (a bisphosphonate, melamine and urea) on the flame retardancy of cotton fabrics treated with phosphorus-doped silica coatings derived from sol-gel processes has been investigated. The hybrid phosphorus-doped silica coatings turned out to synergistically act with 1-hydroxyethane 1,1-diphosphonic acid, while a simply additive effect occurs when the hybrid phosphorus doped silica coatings are further doped with N containing molecules such as melamine or urea. Indeed, silica and bisphosphonate are able to cooperate in the char formation, as shown by thermogravimetry, flammability and cone calorimetry tests. This finding can be probably ascribed to the decomposition of the bisphosphonate (at ca. 260 °C), which gives rise to acidic species that catalyze the cellulose dehydration, meanwhile the hybridphosphorus silica coating, acting as a thermal insulator, further helps in the formation of an aromatic char resistant to the flame propagation.

9.4.6 Intumescent Systems

The intumescent coatings, obtained from a combination of different products, are used to prevent burning and to protect materials, in order to avoid structural damages during fires. The coatings are applied on the material surfaces and they expand with heat, forming a protective insulating layer. Intumescent additives should provide the charred phase together with a swelling agent.

Table 9.3 Field of applications and effects on the combustion process of the main flame retardants

Product	Effect on combustion process
Antimony-based compounds	Flame retarding during the combustion and propagation phases. They work especially in combination with halogens forming antimony trihalide to scavenge free radicals and increase char formation
Boron-based compounds	Flame retarding during the decomposition phase. They are generally char producers ant the heat required from dehydration also contributes to its fire retardant capability. Zinc borate compounds reduce smoke production
Bromine-based compounds	Used with an antimony synergist, they act in the condensed phase to direct chemical reactions inside burning. Heavy-bromine gases cover the material from touching oxygen and heat
Halogenated compounds	Function primarily by a vapour phase flame inhibiting mechanism through radical reaction
Organic nitrogen compounds	Flame retarding during the decomposition phase, they aid in char formation. In combination with phosphates they achieve a phosphorus-nitrogen synergism
Metal hydroxides ($Mg(OH)_2$, $Al(OH)_3$)	Flame retarding during the combustion and propagation phases. More effective as hydrated compounds, they provide flame retarding effects by releasing contained water at high temperatures, absorbing heat from the combustion zone, producing char, generating metal oxide coating that acts as insulator and reduces smoke
Phosphorous compounds	Inorganic phosphorus: flame retarding during the decomposition phase Organic phosphorus: generation of solid form of phosphoric acid inhibits access to oxygen and shields it from releasing flammable gases able to feed flames
	Nitrogen increases the flame retardant effect of organic phosphor compounds. The high nucleophilic character of nitrogen and the high electrophilic character of phosphorus in flame-retardant chemicals are important conditions for the achievement of an effective nitrogen/phosphorus synergy

In general, the formulation of an intumescent system requires three components:

- an acid source: an inorganic acid, acid salt or other acid;
- a carbonizing agent (i.e.: carbohydrate);
- a blowing agent, which decomposes and releases gas, leading to expansion of the polymer and the formation of a swollen multicellular layer (e.g.: amine, amide, melamine, urea, etc.).

Their action is based on the dehydration of the carbohydrate compound by acids, and on the swelling of the resulting carbon by the volatile products of degradation of amine, amide and water vapour sourced from dehydration. The blowing agent could also catalyse the dehydration reaction. A critical feature in the choice of the strategy of additivation of a polymer is its ability to produce, by thermal degradation, a thermally stable residue (char). In this case the polymer itself can function as a source of carbon.

Table 9.3 shows an overview of the main flame retardant products with their related effects.

9.5 Flame Retardants (FR) for Textiles

Organic fibers can be flammable (e.g. cotton, wool, man-made fibers), but they do not burn in the same way, because of their chemical, structural and morphological characteristics. Particularly, several variables can affect the burning behaviour of textile materials:

- the fibre material,
- the structure and the nature of the surface,
- preparation, finishing, dyeing,
- soiling,
- combination of textiles,
- the ambient conditions,
- heat conduction.

Moreover, the properties that characterize the burning behaviour of products can be listed:

- flammability,
- the rate of spreading of flames,
- the development of heat,
- shrinkage and melting,
- the development of smoke,
- the formation of toxic gases.

Flame retardants act either as a barrier between flame and foam, or by limiting oxygen supply to fire. The tendency of textile materials to burn is measured by the oxygen index (Oxygen Index, O.I. or Limiting Oxygen Index, L.O.I.), that is the minimum quantity of oxygen necessary to trigger the combustion. In other words,

Table 9.4 Burning properties for a selection of fibers [23, 24]

Fiber	L.O.I. (%)	Temperature (°C)			
		T_g (°C) Glass transition	T_m (°C) Melting point	T_p (°C) Pyrolysis	T_c (°C) Combustion
Acrylic	18.2	85–100	220	290	250
Cotton	18.4			350	350
Triacetate	18.4	172	290	305	540
Polypropylene	18.6	−20	160–170	469	550
Viscose	18.9			350	420
Polyamide 6.6	21.0	50	260–270	403	530
Polyamide 6	21.0	50	210–220	430	450
Polyester	21.0	80–90	250–260	420–450	480
Wool	24.5			245	600
p-Aramid (Kevlar)	29.0	340	560	590	550
m-Aramid (Nomex)	29.5	275	375	410	500
Modacrylic	30	80	240	273	690

L.O.I. is the minimum amount of oxygen which supports burning over a period of 3 min, or the burning of a 50 mm length of the sample. The most important burning properties of a selection of textile fibers are listed in Table 9.4 in order of their limiting oxygen index and corresponding heats of combustion which are relevant to the important maximum flame temperatures and pyrolysis temperatures.

The most important commercial flame retardants can be classified into three categories: flame retardants based on phosphorus (condensed phase mechanism) and halogens (gas phase mechanism), synergistic systems containing flame retardant enhancers (nitrogen-phosphorus and antimony-halogens) and flame retardants with physical effects (alumina, borate). Some of these treatments have serious drawbacks: for instance the use of halogens as flame retardants is restricted because of the toxicity of their combustion gases, whereas although inorganic salts can provide excellent flame retardant properties for cellulose, they have very poor laundering durability.

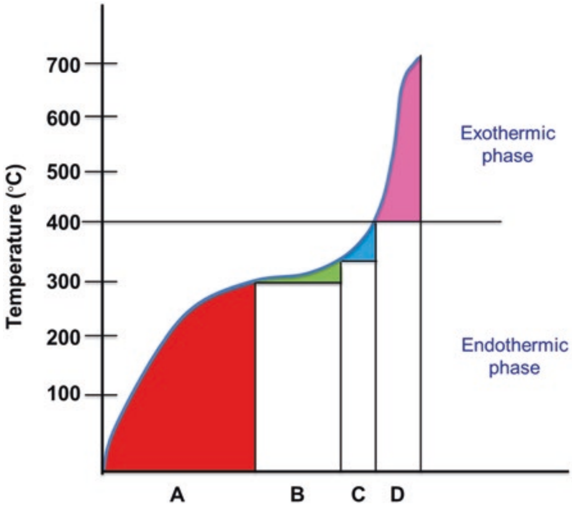
9.5.1 FR for Cotton

Combustion of cotton and other cellulose-based polymers is an oxidation process of the material under heat, which consumes flammable gases, liquids, and solid residues produced in the pyrolysis is of the materials, and results in excess amount of heat.

The combustion process is divided into four stages (Fig. 9.4):

1. heating of the substrate,
2. decomposition (pyrolysis),

Fig. 9.4 Kinetics of combustion of cellulose (*A* heating/decomposition, *B* pyrolysis, *C* ignition, *D* combustion)



3. ignition,
4. combustion (fire propagation).

The heating of the polymer is largely determined by: specific heat, heat conductivity, heat of fusion and heat of vaporization. When the cellulosic material is heated at above 250 °C, the polymer starts its decomposition process resulting in the formation of products like tar (in which levoglucosan, reported in Fig. 9.5, is the major component) flammable gases (methane, ethane and carbon monoxide), nonflammable gases (carbon dioxide and formaldehyde), other by-products (such as water, alcohols, organic acids, aldehydes and ketones), and char. Approximately 51 % water and gases, 47 % tar and 2 % char is formed during the thermal decomposition of cotton fabric [25].

The main pyrolysis stage occurs in the temperature range of 300–380 °C. In this stage larger, heavier molecules are split into simpler, smaller molecules and the weight loss is very fast and significant. The pyrolysis of cellulose is a very complex chemical process and is commonly believed to involve two different mechanisms:

(1) a process of dewatering and charring of cellulose, producing water, carbon dioxide and solid residues;
(2) the production of nonvolatile liquid by depolymerization and by cleavage continues, producing low molecular weight products, which are more flammable.

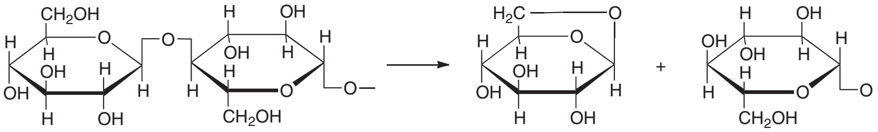


Fig. 9.5 Formation of levoglucosan from cellulose

Only when a combustible gas mixture forms with air is there a danger of fire at the critical pyrolysis temperature. If there is oxygen existing, the decomposed products will be oxidized, generating much more energy and heat to promote more cellulose cleavage.

Finally, during the last stage, in exothermic combustion the released energy contributes to an increase in temperature.

In conclusion, two competitive routes can be drawn for cellulose degradation:

- depolymerisation;
- dehydration.

The former induces the production of levoglucosan giving rise mainly to low molecular weight, highly flammable, species. On the other hand, dehydration gives a carbonaceous residue, known as char. The equilibrium between these processes depends on the heating rate, as recently demonstrated [26].

A wide range of flame retardants for cellulosic materials are available and they can be classified mainly by their washing fastness [2, 13].

Non-durable flame retardants for cellulosics are provide only temporary protection and therefore periodic reprocessing by padding or spraying of an aqueous solution becomes necessary to maintain the flame retardant effect. They are generally water-soluble inorganic salts that are easily removed by water, rain, or perspiration.

The main groups of these flame retardants are based on:

- ammonium salts (i.e. ammonium dihydrogen phosphate and di-ammonium hydrogen phosphate, which have been used for more than 150 years as flame retardants). They are Lewis acids which accept a pair of electrons and act as cellulose dehydrating agents at high temperature. At normal temperatures the salts are inert, but at higher temperatures they decompose into ammonia and phosphoric acid. They decompose at 155–190 °C, below the pyrolysis temperature of cellulose and the phosphoric acid produced catalyzes the dehydration of the cellulose, thus promoting the formation of char and water;
- boron derivatives, like boric acid and borax, sometimes in conjunction with ammonium salts of sulfuric and phosphoric acid, urea, and ammonium bromide;
- diguanidine hydrogen phosphate or monoguanidine dihydrogen phosphates are also examples of inexpensive phosphates for non-durable cotton treatment;
- metallic salts, like $ZnCl_2$, can also be considered as non-durable flame retardant agents, and their action is based on acidity released at the ignition temperature of the cellulose;
- carbonates, halides, and highly hydrated salts that decompose or sublime on heating, releasing large amounts of nonflammable gases that dilute the flame [9].

Cellulosic fibers treated with semi-durable flame retardants should withstand a limited number of washes. Direct application of insoluble salts has its limitations and best results occur by internal precipitation after application of a reagent solution. Other semi-durable treatments involve reactions with polymer. For example heating cellulose with phosphoric acid or ammonium phosphates to temperatures where development of water occurs, a cellulose phosphate will be obtained by phosphorylation on the $HOCH_2$– groups of the glucose units. Cellulose polymer is damaged by acid-catalyzed hydrolysis, consequently the treated fabric loses its tear strength and becomes dark yellow. The damage can be reduced by buffering the acidity of the treatment. It was found that if urea is applied to the fabric with the phosphoric acid or with ammonium salt, the phosphorylation process proceeds more gently and tolerably. In this way, useful flame-retarded cotton fabric can be obtained, with minimum change in colour and good washing fastness [27]. Alkaline laundering conditions remove semi-durable finishes because they destroy the flame retardant both by cleavage of the phosphate-to-cellulose bonds and by ion-exchanging sodium cations for acid hydrogen or ammonium. If the laundering is in water rich of Ca^{2+} and Mg^{2+} (hard water), the cations can also be collected by the phosphate groups and further spoil the flame retardant action by the same mechanism. Finishes thus deactivated can sometimes be partly restored to activity by oxalic acid (“laundry sour” process) to remove the alkali or alkaline earth cations [27].

Cotton samples treated with durable flame retardants should withstand a higher number of washing cycles. The first available finishing agents are based on phosphonium salts THPX having the general formula:

$$\left[(CH_2OH)_4P^+\right]_n X^{n-}$$

where X^{n-} is commonly Cl^-, OH^-, or SO_4^{2-}. The most important product is tetrakis (hydroxymethyl) phosphonium chloride (THPC). The chloride (THPC) is generally preferred relative to other salts, such as the sulphate (THPS), because as a univalent anion, the salt-urea complex achieves a higher degree of penetration into the fiber microstructure. THPC is a water-soluble and storage-stable compound, prepared as a crystalline solid from phosphine, formaldehyde and hydrochloric acid at room temperature, according to the following reaction (Eq. 9.17):

$$PH_3 + 4CH_2O + HCl \rightarrow (HOCH_2)_4P^+Cl^- \qquad (9.17)$$

THPC is a reducing agent and reacts with many other chemicals containing active hydrogens (e.g. N-methylol compounds, phenols, polybasic acids, and amines) to form insoluble polymers on cellulose substrates. The chemical and processing steps for THPC-urea (Proban® process), which requires an ammonia cure and a final oxidative stage, is shown in Fig. 9.6.

THPX is pre-reacted with urea and the solution then adjusted to a pH 5–8 before padding onto cotton. The impregnated fibers are then dried and treated with gaseous ammonia in a specially designed ‘ammoniation chamber’ which crosslinks the finish. At this point, the structure of the finish is probably mainly a network of N–CH_2–P linkages where the phosphorus is still in the lower state of oxidation (organophosphine). It can be stored in air to allow the phosphorus to oxide to the very stable phosphine oxide, or more practicably, treated with hydrogen peroxide to rapidly accomplish the same oxidation.

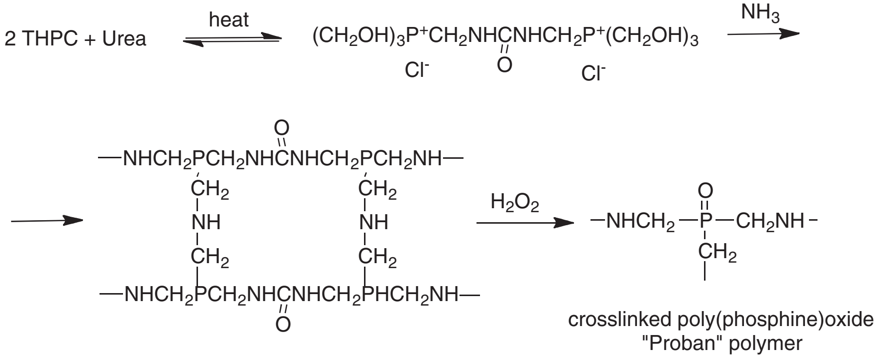


Fig. 9.6 Chemistry of the THPC-urea-NH_3 process

The end product has no hydrolyzable links adjacent to the phosphorus, which is entirely in the very stable phosphine oxide structure and the finish is durable to 100 industrial launderings with alkaline detergent. Moreover, good stress-relieving flexibility and good tear strength are obtained since there is no chemical reaction between finish and the cellulose. When the treated fabric is exposed to flame, it chars and does not melt or exhibit flame spread. Two limiting features for this process are the requirement for a special gas-chamber and that the range of cotton dyes is limited and generally vat dyes, which are compatible with the reducing and oxidizing conditions, must be used. Although the process using THPC is highly effective, it has a number of limitations: the fabrics are stiff;

- tensile and tear strengths are severely reduced;
- there is susceptibility to acid and basic hydrolysis;
- there is release of free formaldehyde during the process;
- small amounts of free or loosely bound formaldehyde are suspected of being able to form bis (chloromethyl) ether, a volatile carcinogen, which must be avoided in the work space.

A competitive compound to the previous ones is [3-[(Hydroxymethyl) amino]-3-oxopropyl]-phosphonic acid dimethyl ester, although more generally it is often called N-methylol dimethyl phosphonopropionamide.

The acid-catalyzed treatment involving this compound with trimethylol melamine (TMM), is called Pyrovatex CP® (Fig. 9.7).

The TMM, added to increase the nitrogen content for the synergistic effect with the phosphorus, is a water-soluble product and reacts with cotton under acid-catalyzed conditions to produce "aminal" linked structures mostly on the 6-hydroxyl groups of the cellulose, and it is normally used to achieve an acceptable level of fixation to the cotton.

The observed acid hydrolysis on storage can be minimized by neutralization of the fabric after curing. This finishing can survive 50 or more launderings, although it is sensitive to hypochlorite bleach treatment and it is not performing as THPX.

A phosphorus-rich oligomeric alcohol-terminated methylphosphonatephosphate (Fig. 9.8) has been proposed, in combination with dimethyloldihydroxyethyleneurea

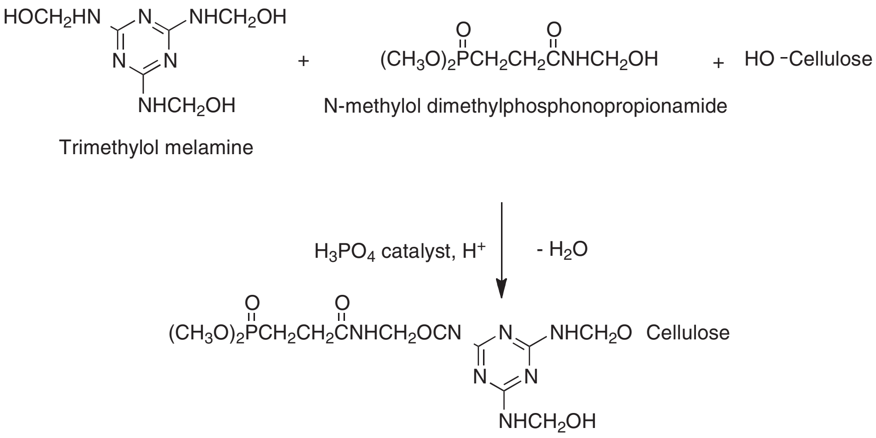


Fig. 9.7 Chemistry of cellulose finishing by Pyrovatex CP® process

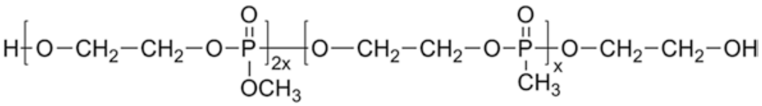


Fig. 9.8 Chemical structure of phosphate-phosphonate flame retardant

(DMDHEU) or trimethylolmelamine, to obtain a flame retardant finish durable to at least 25 washing cycles [28].

If compared to the others flame retardants, this finishing shows the following advantage:

- low formaldehyde content,
- low damage to fabric strength.

An oligomeric vinyl phosphonate finishing was also developed, and its major difference from the other flame retardant finishings is that it is made in an insoluble form by a free radical mechanism, proposed as following (Fig. 9.9):

The compound is water-soluble and is used with methylol-acrylamide and a free-radical catalyst, e.g. persulfate, with a conventional pad-dry-cure-wash procedure at 150–175 °C. The treated fabrics also exhibit wrinkle recovery and durable press properties. It has been applied to cotton polyester blends with the acrylamide or TMM co-reactant. Bromine derivatives have also been added.

9.5.2 FR for Wool

Within the area of flammability of all so-called conventional fibers, wool has the highest inherent non-flammability. Heating the polymer, the first step in

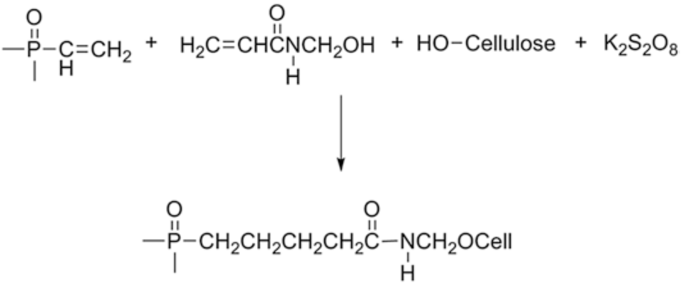


Fig. 9.9 Chemistry of cellulose finishing by oligomeric phosphonate containing vinyl groups

decomposition is the loss of water after that, at around 160 °C, some cross-linking of amino acids occurs. Between 210 and 290 °C, the disulphide bond in the amino acid cystine is cleaved producing carbon disulphide and carbon dioxide. Large amounts of hydrogen cyanide, benzene, toluene, and carbon oxides are obtained from pyrolysis at higher temperatures (600–925 °C).

In some constructions, due to its relatively high LOI value, wool felt is claimed to serve as a fire resistant layer. However, for technical use it needs to be treated by flame retardant finishing. A non-durable finishes based on boric acid–borax (1:2, w/w) mixtures and sulphamic acid (as the ammonium salt) and phosphor compound are commonly used, although the best known treatment is Zirpro®, asaltofzirconiumhexafluoride (Fig. 9.10).

These products can be applied by exhaustion and padding under acidic conditions (pH < 3) to maximize the penetration of the molecule in the polymer and to make the treatment resistant to cleaning cycles (more than 50 both in dry and in water at 40 °C).

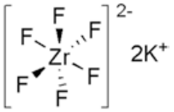
The chemistry of the application can be summarized as in (Eqs. 9.18 and 9.19):

$$\text{Wool-NH}_2 \underset{-\text{H}^+}{\overset{+\text{H}^+}{\rightleftarrows}} \text{Wool-NH}_3^+ \tag{9.18}$$

$$2[\text{Wool-NH}_3^+] \underset{-[\text{ZrF}_6]^{2-}}{\overset{+[\text{ZrF}_6]^{2-}}{\rightleftarrows}} [\text{Wool-NH}_3^+]_2\,[\text{ZrF}_6]^{2-} \tag{9.19}$$

The complex of heavy metals anions mainly forms ionic bonds with the fiber, as well as dyes, and the flame-retardant effect is due to the zirconium which increases the formation of carbonaceous residues. The finishing is solid to dry cleaning and washing in water up to 40 °C and with a maximum pH of 6. Applications at higher pH could give zirconium oxide which is ineffective for treatment.

Fig. 9.10 Chemical structure of zirconiumhexafluoride potassium salt



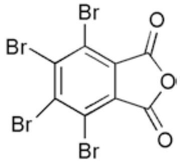


Fig. 9.11 Chemical structure of tetrabromophthalic anhydride (TBPA)

Moreover, tetrabromophthalic anhydride (TBPA, Fig. 9.11), which produces the carboxyl form by hydrolysis in aqueous solution, represents another flame-retardant finishing for wool.

The combination of TBPA with the Zirpro treatment is used to reduce after-flaming times and minimise heat release [29]. Finally, some combinations of salts of polyethyleneimine with aminomethylphosphonic acid are used as flame retardant finishing of wool and its blends, due to their washing fastness [30, 31].

9.5.3 FR for Polyester

Polyester fibers are very easily ignitable, especially when they are blended with cotton fibers. It burns strongly and may drip, carrying flames to other surfaces. In fact, the molten material can form drops act as a second source of ignition and cause more rapid development of the fire.

Thermal decomposition of polyesters is a complex process with activation energies varying from 100 to 250 kJ/mol and, although its thermoplastic polymer contains aromatic structures in their chain, they are very combustible. The scission of the polymer chain through a six-membered ring transition stage is usually the first step of the thermal decomposition of polyesters. Although the mechanism is still under investigation, probably this scission is mostly heterolytic and not a free-radical process. Other reactions mostly involve the formation of vinyl ester chain ends which lead to polyene structures, crosslinking, and also evolution of light volatile molecules. To improve fire retardant properties of polyester it is possible to modify the mechanism of its thermal decomposition. Upon combustion or high temperature decomposition polyethylene terephthalate (PET) generates some smoke composed of terephthalic and benzoic acid derivatives, low molecular weight oligomers, and polycyclic aromatic hydrocarbons [32].

The presence of chemical finishes and dyes that can affect the combustion-melting phenomenon of the fibers could lead to an easier ignition. Polyester can achieve flame retardant properties by three possible approaches, by using phosphorus or bromine-containing compounds:

(1) incorporated as co-monomers in the polymer matrix;
(2) added during the extrusion;
(3) used as finishing.

The first two methods would give inherently flame-retardant polyester fibres. The most important commercial flame retardant additives for polyester fibers are:

- ethoxylated tetrabromobisphenol A comonomer;
- tris(2,3-dibromopropyl) phosphate;
- cyclic phosphonate ester;
- 2-carboxyethyl(methyl)phosphinic acid.

Particularly, the L.O.I. of polyester polymer copolymerized with 2-carboxyethyl (methyl) phosphinic acid (Trevira® CS), using 0.6 % w/w phosphorus, is 28 % and the burning sample does not drip.

Flame retardant property can also be achieved by thermosol process, with a treatment similar to the thermosol dyeing realized by disperse dyes. In this treatment, the fibers soften and become permeable during cure at about 190–210 °C for 30–40 s. In this stage the flame retardant finish, previously applied by padding, migrates into the fibers and, then after cooling, it is tightly fixed.

Although triphosphonate has been shown to be a good flame retardant, various phosphate esters, such as tetraphenyl resorcinol diphosphate, have shown success as melt additives in polyester [27]. One of most used product in the polyester fibers treatment is a liquid phosphonate of the following structure (Fig. 9.12):

In the above formula, if “x” is:

- 0, the related triphosphonate can be used as a melt additive in polyester fiber prior to spinning;
- 1, the product can be used in the thermosol treatment.

A thermosol treatment of polyester fabric can also be done using hexabromocyclododecane (Fig. 9.13) applied as an aqueous suspension or emulsion, drying and then taking the fabric to 180–205 °C for a short period, thereafter removing excess flame retardant by washing or scouring. This finish is said to be effective not only on polyester but on low melting fibers, such as polypropylene and also on nylon.

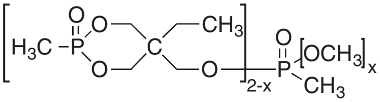


Fig. 9.12 Chemical structure of phosphonate for polyester treatment

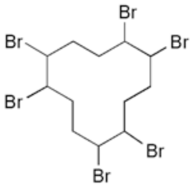


Fig. 9.13 Chemical structure of hexabromocyclododecane

9.5.4 FR for Polyamide

Polyamides macromolecules, having repeating units containing the characteristic group –CO–NH–, can be classified into three main groups:

- natural polyamides (e.g. wool, silk, and leather);
- aliphatic nitrogen-containing synthetic polymer;
- synthetic aromatic polyamides (of exceptionally high thermal stability and used for protective clothing).

As a class, polyamides do not notably decompose below 342 °C. More specifically, due to thermal decomposition:

- polyamide 6 produces small amounts of various simple hydrocarbons;
- polyamide 6–6 melts between 255 and 260 °C, and decomposition begins at 340 °C in air and 420 °C in nitrogen. Carbon dioxide and water are the principal gaseous products of decomposition of this polyamide;
- polyamide 6–10 produces notable amounts of hexadienes and hexene;
- aromatic polyamides have good thermal stability. Nomex is stable in air to 450 °C, for higher temperature the main product of its decomposition are benzene, benzonitrile, carbon monoxide, hydrogen cyanide and toluene. Above 550 °C, hydrogen and ammonia are formed, while the remaining residue is highly cross-linked [33].

For the aliphatic polyamides, nylon 6, and 6.6, no effectively durable flame retardant exists. Flame retardant treatment scan be performed by adding suitable chemicals into the polymer matrix or on to the fabric surface. The most common additives are bromine-based, while the main products for the superficial treatment contain phosphorus, formaldehyde and urea. Effective application is made by back-coating with antimony trioxide (Sb_2O_3) and bromine-releasing molecules (e.g. decabromodiphenyloxide: DBDPO), whose respective molecules are shown in Fig. 9.14.

To obtain an acceptable wash-durable finish, a thiourea-formaldehyde oligomer pre-condensate ($NH_2C(=S)NH[CH_2–NH–C(=S)NH]_nCH_2OH$ plus an acid catalyst) can be also applied to create a cross-linked resin structure, with possibly some binding to the amide groups of the nylon. This finish probably works by stimulating melt flow and drip [34].

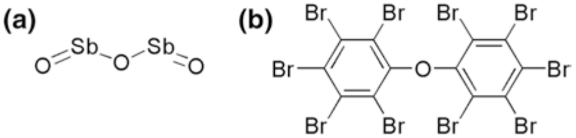


Fig. 9.14 Chemical structure of antimony trioxide (**a**) and of decabromodiphenyloxide (**b**)

9.5.5 FR for Polypropylene

Due to its aliphatic hydrocarbon structure, polypropylene by itself burns very rapidly with a relatively smoke-free flame and without leaving a char residue. It has a high self-ignition temperature (570 °C) and a rapid decomposition rate compared with wood and other cellulosic materials and hence has a high flammability [35]. During the heating of Polypropylene a decrease in molecular weight is observed at 230–250 °C, while volatilization becomes significant above 300 °C. At a surface temperature of 340 °C the ignition of Polypropylene due to radiative heating has been observed.

The flame retardancy of polypropylene may be achieved by:

- promoting the formation of a carbonaceous char which will block heat (changing pyrolysis reactions and reducing the volatile formation to protect the polymer from further oxidation);
- using halogen based additives to inhibit the initiating radicals in the pre-flame and flame zones;
- adding some hydrated inorganic additives that release water during their endothermic decomposition, thus withdrawing heat and diluting the combustible volatiles;
- modifying the chemical structure of the macromolecule to change its decomposition;
- adding a char-forming additive with intumescent property.

Apart from antimony–halogen or in some cases, tin–halogen formulations only one single flame retardant system, tris(tribromoneopentyl) phosphate, is presently effective in polypropylene when required for fibre end-uses. Currently, it is the most promising flame retardant additive which is usefully effective and thermally and light stable enough for melt spinning in polypropylene. Finally, grafting of pentabromobenzyl acrylate during polypropylene melt processing has been suggested to obtained flame retardancy with good launderability and color stability [36].

9.6 Flame Retardant Testing Methods

Different instrumentations can study different properties of textile products with or without fire-resistant properties. The testing methods commonly used today in both industry and research laboratory include fabric vertical flammability testing method (UL94), limiting oxygen index (L.O.I.) method, and thermogravimetric (TG) analysis technique.

The UL94 vertical burning test is a widely used fire test for industrial polymeric materials and products [37]. The standard includes several test methods that are employed depending upon the intended end-use of the material and its orientation in the device. The standard outlines two horizontal burning tests, three vertical burning tests, and a radiant panel flame spread test. The most commonly used method is summarized below as a typical example of a flammability test. In this test, the Bunsen flame is applied to a specimen measuring 125 mm in length by 13 mm wide are suspended vertically and clamped at the top end.

The 20-mm-long flame from a methane burner is applied to the center point on the bottom end of the sample. The burner is positioned such that the burner barrel is located 10 mm below the bottom end of the textile specimen and removed after 10 s of flame application.

When the flame of the polymer specimen extinguishes, the Bunsen burner is applied for another 10 s. The specimen is rated mainly according to the recorded flaming time of the specimen as well as the mass loss rate and the dripping behaviors.

According to IEC 60695-11-10 Vertical Flame standard test, the specimen is classified as V-0, V-1 or V-2 as following (Table 9.5).

The test can be carried out with specimen in a horizontal position. In this case, a flame is applied to the end of the specimen for 30 s. To meet industrial requirements as well as to classify the polymeric materials, the UL 94 test is widely used both in industry and in academic research centers. However, due to its basic character, the obtained information by the above mentioned test remains limited.

Table 9.5 UL94 vertical test requirements

Vertical ratings	Requirements
V-0	• Specimens must not burn with flaming combustion for more than 10 s after either test flame application
	• Total flaming combustion time must not exceed 50 s for each set of 5 specimens
	• Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	• Specimens must not drip flaming particles that ignite the cotton
	• No specimen can have glowing combustion remain for longer than 30 s after removal of the test flame
V-1	• Specimens must not burn with flaming combustion for more than 30 s after either test flame application
	• Total flaming combustion time must not exceed 250 s for each set of 5 specimens
	• Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	• Specimens must not drip flaming particles that ignite the cotton
	• No specimen can have glowing combustion remain for longer than 60 s after removal of the test flame
V-2	• Specimens must not burn with flaming combustion for more than 30 s after either test flame application
	• Total flaming combustion time must not exceed 250 s for each set of 5 specimens
	• Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp
	• Specimens can drip flaming particles that ignite the cotton
	• No specimen can have glowing combustion remain for longer than 60 s after removal of the test flame

The L.O.I. test does not provide a reliable indication of material performance in real fires. However, the results appear to be very sensitive to the composition of the material and therefore the test is used as a quality assurance tool of fire-retardant-treated materials.

The L.O.I. test apparatus consists of a glass tube in which the specimen is placed. A gas mixture of oxygen and nitrogen is supplied at the bottom of the tube and a small candle-like flame is applied to the top of the specimen to ignite it. According to ISO 4589-1,2 (or ASTM D2863), the aim of the test is to find the minimum oxygen concentration in the oxygen/nitrogen mixture that will result in sustained combustion for at least 3 min. The L.O.I. value is expressed as in (Eq. 9.20):

$$L.O.I. = \frac{[O_2]}{[O_2] + [N_2]} 100 \tag{9.20}$$

As air contains 21 % oxygen, fibers having L.O.I. values of 21 % or below ignite easily and burn rapidly in air. Those with L.O.I. values above 21 % ignite and burn more slowly and generally when L.O.I. values rise above approximately 26–28 %, fibers and textiles may be considered to be "self-extinguishing", because their combustion cannot be sustained at ambient temperature without an external energy contribution.

Incorrect L.O.I. values can be obtained due to melting and dripping of the polymer during the L.O.I. test. Moreover, specially for man made textiles, the dripping of flaming polymer drops can take the fire away from the sample surface, causing its extinction.

The char yield is determined by thermal gravimetric analysis (TGA) under either air or nitrogen atmosphere. Thick char becomes a better thermal insulating layer, which undergoes slow oxidative degradation and prevents heat reaching the remaining polymer. It was pointed that the chars obtained in the intumescent systems are different from the chars from TGA. The former are prepared at lower temperatures and are not fully pyrolyzed or oxidized, their rate of formation is high and involves thermo-oxidation though they serve the same purpose, namely acting as barriers to the passage of molten polymer and decomposition gases [2].

However, those methods all have various limitations. LOI is a valuable quantitative method to determine a material's ability to ignite, but it is not able to provide other critical information related to the combustion of textiles. Vertical flammability test based on a fabric specimen's char length after a standard burning procedure is probably the most frequently used textile flammability testing method in the industry. But it is not a quantitative method and therefore it is difficult to use this method for evaluating small differences in flame retardant fabric samples. TG is another method commonly used in textile flammability research, but it only provides information related to a textile material's decomposition, not its combustion in oxygen. None of those analytical techniques are able to measure the maximum speed at which its fire can generate heat, i.e. the PHRR (peak heat release rate), commonly evaluated for plastics by cone calorimetry. Recently Cone Calorimeter has been also used to evaluate the heat release rate of textiles although fabrics are a dimensionally thin samples and standardized sample preparation is difficult to perform. The Cone Calorimeter is standardized as ASTM E 1354 (Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter) and as ISO 5660 (Fire Tests—Reaction to Fire—Part 1: Rate of Heat Release From Building Products—Cone Calorimeter Method). Using a truncated conical heater, a 100 × 100 mm sample is exposed to a radiant flux of up to 100 kW/m^2. Piloted ignition is provided by an electric spark. An average of the readings of thermocouples, in contact with the coil, supplies the heater temperature data. The cone calorimeter test enables characterization of such parameters as Time To Ignition (TTI, s), Flame Out time (FO, s), Total Heat Release (THR, kW/m^2), peak of Heat Release Rate (PHRR, kW/m^2), Total Smoke Release (TSR, m^2/m^2), peak of Rate Smoke Release (PRSR, 1/s), Smoke Factor (SF, calculated as PHRR × TSR, MW/m^2) and CO and CO_2 release (ppm and %, respectively).

The burning behaviour of textiles depends on the characteristics of the material, their structure, weave and on many other interrelating factors, including air supply, airflow and the positioning. No two fires are alike which makes the whole subject extremely complex. According to the great variety of end-use textiles there are several test methods, the main specific types are listed in Table 9.6.

Table 9.6 Flame retardant standards for selected application fields

Product	Standard	Comments
Generic	ASTM D-2863	Determines minimum oxygen level to support combustion
	ISO 6940:2004	Measurement of ease of ignition of vertically oriented textile fabrics and industrial products in the form of single or multi-component fabrics, when subjected to a small flame
	ISO 6941:2003	Measurement of flame spread properties of vertically oriented specimens
Clothing	BS EN 1103:2005	Procedure to determine the burning behaviour
	BS EN 531:1995	Workers exposed to heat
	BS EN 532:1995	Protection against heat and flame
Furnishings	EN 1021-1:2006	Assessment of the ignitability of upholstered furniture (ignition source smouldering cigarette)
	BS 6807:1986	Ignitability of mattress and bedding materials
	BS 7177:1996	Specification for resistance to ignition of upholstered furniture (mattresses, divans and bed bases)
Upholstered furniture	BS 5652:1990	Covers beds, sofa-beds, futons and other convertibles, nursery furniture, furniture in new caravans, etc., but not carpets and curtains
Curtains and drapes	BSEN 1101:1996	Burning behaviour of curtains and drapes drapes
	BS 5867-2:2008	Flammability requirements. Specification
Textile floor	BS 4790:1972	Determination of the effects of a small source of ignition on textile floor coverings (hot metal nut method)
	BS6307:1982	Methenamine tablet test
	ISO 6925:1982	Textile floor coverings—burning behaviour
	BS 476 Part 7	Classification of spread of flame

9.7 Environmentally Sustainable Flame Retardants: Novel Approaches

A multidisciplinary approach from the physics to the chemistry of fire is required to replace of existing flame retardants with sustainable and environmentally friendly alternatives for textiles in domestic, safety, transport (automotive, rail, aerospace and marine), civil emergency and military, construction and other industries. Halogenated flame retardant are environmentally persistent and generate toxic, corrosive gases during combustion that threaten both air and water ecosystems. Moreover, formaldehyde commonly used in several flame retardant compounds, is toxic making it undesirable for textile finishing. Finally, health implications and environmental claims associated with antimony trioxide (SbO_3) suggest the development of new flame retardant antimony free. It is not flame retardants on their own but function as a catalyst to speed the release of bromine or chlorine radicals by halogenated flame retardants. Therefore, there is an immediate need to replace these chemicals with more environmentally compatible alternative materials.

In the last years novel approach in the field of textile fabrics flame retardancy has attracted a great interest from both industrial and academic research.

A detailed and competent overview is given by Alongi et al. [14]. Different strategies have been designed and, in particular, three approaches have shown the most interesting results: (i) the nanostructuring of the synthetic fibres, (ii) the introduction of nanoparticles in the traditional back-coating and (iii) the deposition of (nano)coatings.

Alongi et al. demonstrated that it is possible to confer enhanced flame retardancy properties to both synthetic (i.e. polyester) or natural (i.e. cotton) fabrics and their blends through the formation of a nanosized coating. By this route, an inorganic shield, potentially capable to protect the underlying polymer from heat, oxygen and flame, is deposited on the fibre surface. Indeed, the nano-coating can act as a thermal insulator absorbing the heat and oxygen from the atmosphere and blocking their transfer to the surrounding polymer. At the same time, the coating can entrap the volatile species produced by the substrate that can further fuel the combustion. Hence, the substrate is protected and tends to pyrolyse instead of burning. These nanosized finishes (i.e. aluminium hydroxide, organoclays) are typical examples of non-halogenated, environmentally friendly, flame retardants. In particular, polymer nanocomposites do not only enhance the fire retardancy but also the mechanical properties, due to a high interphase specific area between nanometric filler and hosting matrix. These materials exhibit enhancements in a variety of physical properties at one tenth the loading required as compared to when micrometer size additives are used [38, 39].

It was also found that that the addition of relatively small amount of silicon compounds to various polymeric materials can significantly improve their flame retardancy, through both char forming in the condensed phase and the trapping of active radicals in the vapour phase [40].

Polyhedral oligomeric silsesquioxane (POSS) reagents, monomers and polymers are emerging as a new chemical feedstock technology for the preparation of nano-reinforced materials [41]. POSS reagents form a class of three-dimensional oligomeric organosilicon compounds of the general formula $(RSiO_{1.5})_n$, where n is an even number and R can be any of a large number of groups (typically methyl, halogen, vinyl or phenyl) [2].

On combustion of such a polymer composite, POSS acts as a precursor forming thermally stable ceramic materials at high temperature. Instead, bohemite nanoparticles could behave like an efficient flame retardant because of their endothermic decomposition accompanied by the release of water, resulting in cooling and dilution effects. Alongi et al. [41] demonstrated that these nanoparticles turn out to play a protective role on the thermo-oxidation of the cotton, modifying its degradation profile. Indeed, POSS and bohemite nanoparticles are able to enhance the thermal stability of cotton in air favoring the mechanism of carbonization and, thus, increasing the final residue at high temperatures, slowing down the overall thermo-oxidation kinetics. The main result is the formation of a carbonaceous surface char that acts as a physical barrier toward the heat and oxygen transfer to the polymer.

Layer by layer (LbL) assembly can be considered as an evolution of the nanoparticle adsorption process [42].

This technique consists in a wash-alternate immersion of the textile sample into an oppositely charged polyelectrolyte solution. The process leads to a total surface charge reversal after each immersion. It then creates a structure of positively and negatively charged layers piled up on the substrate of the surface. Due to the electrostatic attraction between each layer, the resulting interactions are very strong and independent from the substrate size and topology.

The LbL assembly through electrostatic interactions simply requires the alternate immersion of the substrate into an oppositely charged polyelectrolyte (usually water-based) solution (or dispersion). Thus, an assembly of positively and negatively charged layers piled up on the substrate surface is obtained, exploiting a total surface charge reversal after each immersion step. Carosio et al. [43, 44] have exploited LbL process in order to enhance the flammability resistance and to solve the dripping of PET, one of the most important issues for an industrial application of this fabric. The treatment tested with a vertical flame spread test (ASTM D6413 standard) was able to reduce the burning time by 95 % and to eliminate melt dripping phenomena. All the results achieved in the last 3 years exploiting the LbL assembly have highlighted that the successful key for imparting flame retardancy to both natural and synthetic fibres is the production of char. For this reason many researches were focused to realize novel complex architectures having a char-forming character appropriate for both natural and synthetic fibres cotton, polyester and their blends [45].

Referring to LbL assemblies also spraying could represent an appealing alternative to dipping because of its efficiency and feasibility at an industrial scale. The results collected up-to-now have shown that both dipping and spraying allow achieving the same high level of uniformity of the deposited film [46].

Recently the sol-gel processes have been exploited in textile field for conferring multifunctional properties [47]; in particular, great attention has been devoted to the development of "smart" textiles exhibiting antimicrobial or UV radiation protection [48], dye fastness [49], anti-wrinkle finishing [50], hydrophobicity [51], biomolecule immobilization [52], photocatalytic properties [53] and sensor characteristics [54, 55].

In the last years, sol-gel architectures have been shown to be able to protect the polymer surface exerting a thermal shielding effect, thus improving the flame retardancy of the treated fabrics [56, 57].

Particularly, the concurrent presence of P and Si elements in the same precursor can be exploited for preparing hybrid organic-inorganic coatings that behave, at the same time, like char promoters (because of the phosphoric-acid source) and thermal shields (due to the inorganic ceramer). This finding may be exploited for improving the flame retardancy properties of a polymer or copolymer, as recently investigated [19, 58, 59].

Moreover, the exploitation of dual-cure processes that involve a photopolymerisation reaction and a subsequent sol-gel process represents a versatile route, by which it is possible to synthesise hybrid organic-inorganic architectures. These latter are able to enhance the flame retardancy of cotton [60]. Moreover, sol-gel and dual-cure processes are able to create coatings covalently linked to the cotton cellulose and so their derived architectures can be considered as a semi-durable or durable treatment, depending on the used standard to assess the washing resistance.

Generally speaking, the possibility of using green flame retardant systems for replacing the traditional chemicals continues to stimulate the industrial and academic research efforts toward innovative solutions. With the aim to use of halogen- and formaldehyde-free flame retardant systems based on natural macromolecules, the properties of proteins or nucleic acids were investigated. Alongi et al. have recently demonstrated that it is possible to enhance the flame retardancy of cotton fabrics by using caseins and hydrophobins [61] and nucleic acids [62, 63]. The results, at the end of horizontal flame spread tests, have shown a high residue while the burning rate was drastically reduced. This technique has been developed in the last years and, therefore, there are no real examples concerning the possible industrial scale-up in textile field. However, there is a good chance that the above discussed technologies can be used in the textile industry. In fact the innovative chemicals can be applied by conventional equipments for textile finishing, such as impregnation, exhaustion or spray. Finally, polycarboxylic acids have been also used to reduce the flammability of textile fabrics [64]. Although the system has not been fully studied yet, the polycarboxylic acid-based fire retardant finish seems to achieve high levels of the flame retardant performance and washing fastness using, by relatively low add-on levels on the fabric. The main work in this field is in char-forming polycarboxylated species like butyl tetracarboxylic acid (BTCA) along with other functional species that may interact with cellulose to generate acceptable levels of flame retardancy for certain textile fabrics with moderate levels of durability to washing [3].

9.8 Conclusion

The comparison of main flame retardant mechanisms has shown how the choice of an application process could result in different problems and/or challenges for the flame retardant performance of textile polymers. Moreover, hazardous chemicals, multi-step application processes and formaldehyde emissions during curing and after finishing are cost and environmental problems to be solved. It is quite predictable that both voluntary measures and prohibitive legislation will significantly diminish the use of halogenated flame retardants or formaldehyde-based compounds. In fact, the increasing pressure to replace toxic chemicals have yet increased the investigation on halogen- and formaldehyde-free fire resistant materials, as described in this chapter. It should be remembered, however, that the potential environmental impact of the production and use of such new materials should also be assessed holistically, including the raw materials and manufacturing processes used to make the chemicals, as well as the recyclability of the material at the end of the product's life.

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Chapter 10
Flame Retardant of Cellulosic Materials and Their Composites

Amina L. Mohamed and Ahmed G. Hassabo

Abstract Three main topics are described in this chapter, namely (i) physical and chemical structural of cellulosic materials, (ii) fire and flame retardancy finishing of cellulosic materials, and (iii) fire and flame retardancy finishing of cellulosic materials and its composite. The first subject describes in detail different cellulose sources and their chemical and physical structures. Furthermore, the types, structure, and chemical composition of different fibers (cotton, linen, jute, bamboo, hemp, and wood) and their blend have been described in detail. The second subject contains the uses of flame retardant fabrics, and describes the deference in the definition of retardant/resistant terms; in addition, the theory of combustion or burning process, and the mechanism of fire and flame retardant action are explained in detail. Also, different phosphorous flame retardant synergism, types of flame resistant finishes, and their classification based on durability and nature have been mentioned. By the end of this chapter, different Flammability Tests for Textile are described in detail. The last section of the chapter shows the finishing of cellulosic materials and their composites in detail.

10.1 Physical and Chemical Structural of Cellulosic Materials

10.1.1 Sources for Cellulose

Cellulosic fibres are natural polymers of vegetable origin, like cotton, linen, jute, ramie, hessian and sisal. So, it would be useful to study the chemical and the physical structure of these natural polymers.

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Cellulose is found in plants as micro-fibrils (2–20 nm diameter and 100–40,000 nm long). These form the structurally strong framework in the cell walls. Cellulose is mostly prepared from wood pulp. Cellulose is also produced in a highly hydrated form by some bacteria (for example, Acetobacter xylinum) [1].

10.1.2 Structural Unit

In the plant kingdom, cellulose is an important structure material [2]. It is the main construction material of the plant cell walls that are made out of it [3]. Native cellulose occurs in plant (such as cotton and ramie which contain a highly pure cellulose, as lignocelluloses) and in bast fibres (such as flax, hemp, jute and wood) where it occurs in combination with lignin, homocellulose [4].

Cellulose is a linear polymer of β-(1 → 4)-D-glucopyranose units often the so-called $^4C_1$ chair conformation. This is illustrated in Fig. 10.1 where the ring oxygen is at the back, the 4-carbon is 'up' and the 1-carbon is 'down'. Conversely, furanose rings can oscillate and have a more flexible structure than pyranose rings, which means that they are less likely to have a fixed interaction with a molecule of water as energy will be lost in this process. The fully equatorial conformation of β-linked glucopyranose residues stabilizes the chair structure, minimizing its flexibility (for example, relative to the slightly more flexible α-linked glucopyranose residues in amylose).

10.1.3 Molecular Structure

Cellulose is an insoluble molecule consisting of between 2,000–14,000 residues with some preparations being somewhat shorter. It forms crystals (cellulose I_α) where intra-molecular (O3-H → O5′ and O6 → H-O2′) and intra-strand (O6-H → O3′) hydrogen bonds holds the network flat allowing the more hydrophobic ribbon faces to stack. Weak C6-H → O2′ hydrogen bonds may also make some contribution to the crystal stability. Each residue is oriented 180° to the next with the chain synthesized two residues at a time. Although individual strand of cellulose are intrinsically no less hydrophilic, or no more hydrophobic,

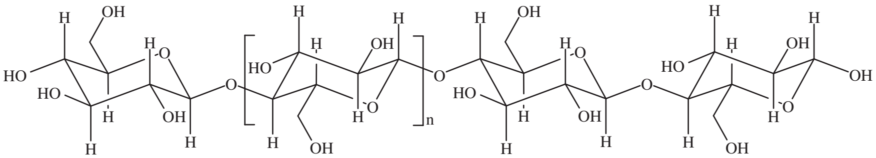


Fig. 10.1 Chemical structure of cellulose

than some other soluble polysaccharides (such as amylose) this tendency to form crystals utilizing extensive hydrophobic interactions [5] in addition to intra- and intermolecular hydrogen bonding makes it completely insoluble in normal aqueous solutions (although it is soluble in more exotic solvents [6] such as aqueous N-methylmorpholine-N-oxide (NMNO, ~0.8 mol water/mol, then up to 30 % by weight cellulose at 100 °C [7]).

Moreover, these crystal regions are responsible for the limited solubility of cellulose and make it difficult for solvents and reagents to access areas within the cellulose fibres. It is thought that water molecules catalyse the formation of the natural cellulose crystals by helping to align the chains through hydrogen-bonded bridging, as shown in Fig. 10.2 [8].

10.1.3.1 Molecular and Supramolecular Features of Cellulose

The chemical composition of cotton fibres has been reported in detail in several studies before [9, 10]. The cotton consists of an assembly of cellulose chains connected via inter-chain hydrogen bonding. Cellulose makes up 95 % of the cotton fibre after ginning. The secondary wall, which is almost entirely cellulose, consists of crystalline cellulose in multiple layers, called micro-fibrils.

Cellulose is a complex composite material, which structurally comprises three hierarchical levels: (i) the molecular level of the single molecule; (ii) the supermolecular level concerning the packing of the molecules in crystals called microfibrils; and (iii) the morphological level. Figure 10.3 illustrates the arrangement of micro-fibrils and interstitial voids in relation to the cell wall [7].

Plant cell walls are constructed from a combination of a variety of polysaccharides that can be generally grouped into cellulose, hemicelluloses, and pectic polysaccharides (Fig. 10.3), and whose relative proportions depend on the plant species, specific tissue, and growth stage. Cellulose, the most abundant structural polysaccharide in cell walls (comprising 15–50 % of the dry weight of plant biomass).

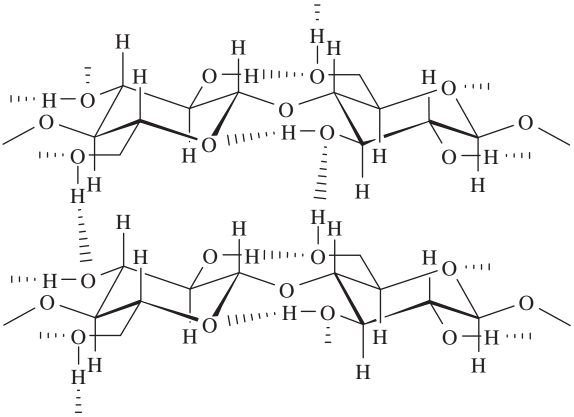


Fig. 10.2 Unit cell of the crystal lattice of cellulose in the cotton fibre

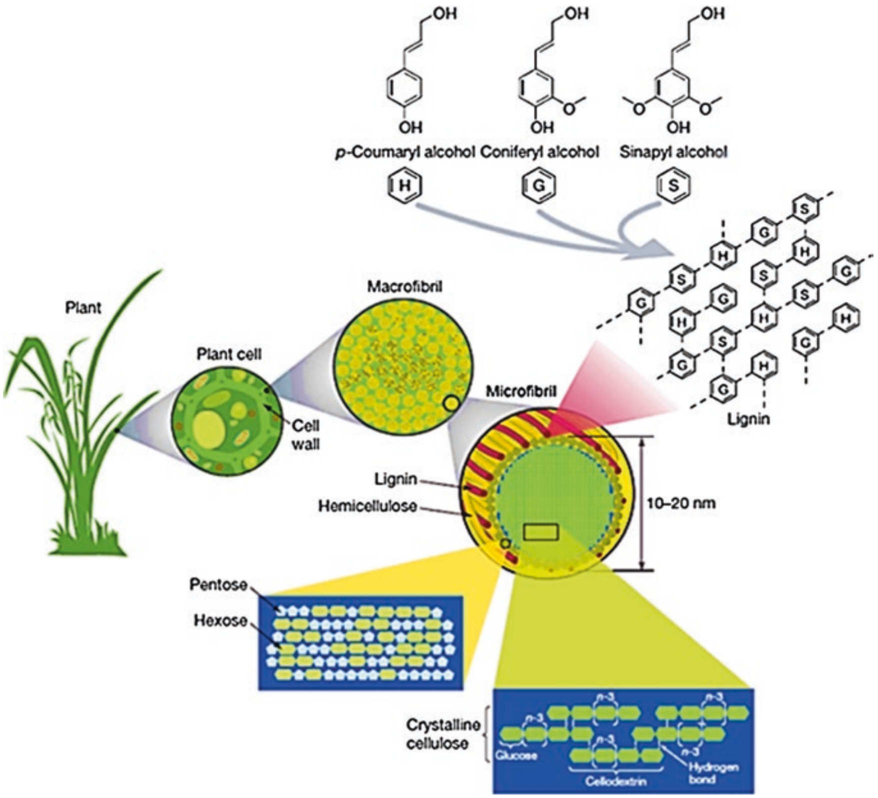


Fig. 10.3 Interpretation of cotton wall structure [11, 12]

The macro-fibrils consist of numerous micro-fibrils of cellulose interspersed by micro-porosities containing non-cellulosic wall materials. Micro-fibrils consist of bundles of cellulose molecules, partly arranged into micelles. Micelles are crystalline because of regular spacing of glucose residues which are connected by β-1,4-glucosidic bonds [11].

10.1.3.2 Chemical Structure of Cellulose

Haworth has proposed that the structural formula of sugars be written in a roughly three-dimensional prescriptive manner, which when applied to cellulose yield the formula in Fig. 10.1. Furthermore, it is a polysaccharide made up of β-D (+) glucose residues. These molecules condensed and linked together linearly by means of 1-4, β-glucosidic bonds [13–15].

Each repeating anhydroglucose unit has three reactive hydroxyl groups, so they are polyhydroxyl alcohols [14, 16]. Two of these groups in the position 2 and 3 are secondary hydroxyl groups, whereas the last one in the position 6 is a primary hydroxyl group [17]. Cellulose molecules have the opportunity of forming many hydrogen bonds with its primary hydroxyl groups because it is more reactive than secondary hydroxyl group [3, 13]. In addition, the primary hydroxyl group is more acidity than the secondary [17].

Steric hindrance is an important consideration, particularly in the case of bulky reacting species; position 6 is least sterically hindered [3]. Whenever the distance between the various oxygen and hydrogen atoms in the cellulose molecule reaches 3 Å or less, they interact with each other to form intermolecular hydrogen bonding [14].

10.1.3.3 Physical Structure+ of Cellulose

Crystalline and Amorphous Regions

Cellulose has the capability of forming many hydrogen bonds along the length of the polymer chain with its three-hydroxyl groups. These bonds, combined with the other (principally the Van der Waals attraction), bind together, and it is ranging perfect geometrical packing of crystal lattice (crystalline region) to random condition (amorphous region) [13].

Cellulose Accessibility and Reactivity

Reactivity and accessibility have been used to describe the easiness with which cellulose can react. More properly, reactivity of cellulose is the ability of the chain molecules to react with other molecules, whereas accessibility of cellulose defines the ease by which the functional groups of the chain molecule can be by reached the reactant molecule [18, 19].

It has been proposed that the accessibility of cellulose depends mainly on the number and size of the pores in the cellulose structure; the size and type of solvent or reagent; the internal surface, as determined by the size of fibrils or fibril aggregates, that is accessible; and the structure of the cellulose molecules, which will determine which hydroxyl groups are accessible. Therefore, to increase cellulose accessibility, the pores must be opened, and both the fibril aggregates and the highly ordered regions must be altered [20].

10.1.4 Natural Fibres

Natural fibres are composed primarily of cellulose, hemicellulose, and lignin, with the balance being made up of pectins, water soluble compounds, waxes, and inorganic, non-flammable substances, which are generally referred to as ash. Examples of the chemical composition of some plant fibres are shown in Table 10.1 [21].

The decomposition of cellulose, between 260 and 350 °C, results in the formation of flammable volatiles and gases, non-combustible gases, tars, and some char

Table 10.1 Chemical composition of some plant fibers [21]

Fibre	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Ash (%)
Flax	64–71	2–5	18.6–20.6	5
Kenaf	44–57	15–19	22–23	2–5
Sisal	67.5–78	8–11	10–24	0.6–1
Bamboo	26–43	21–31	15–26	5–17
Rice	28–48	12–16	23–28	15–20
Coir	36–43	41–45	0.15–0.25	2 [22]
Deciduous	38–49	23–30	19–26	<1
Coniferous	40–45	26–34	7–14	<1
Cotton	85–90	7–16	1–3	0.8–2

[23–26]. A high content of cellulose tends to increase the flammability of the fibre. Hemicellulose decomposes between 200 and 260 °C but forms more non-combustible gases and less tar than cellulose.

Lignin contributes more to char formation than either cellulose or hemicellulose [27, 28]. Therefore, based only on chemical composition, coir, with a low cellulose (36–43 %) and high lignin (41–45 %) content, and deciduous wood fibre, with a low cellulose (38–49 %), high lignin (23–30 %), and hemicellulose (19–26 %) content, should have lower flammability than, for example, cotton, which has a very high cellulose (85–90 %) content. Lignin starts decomposing from about 160 °C and continues to decompose until about 400 °C. At the lower temperatures, relatively weak bonds break, whereas at higher temperatures, cleavage of bonds in the aromatic rings of the lignin takes place [29].

Manfredi et al. [30] showed the importance of lignin in the thermal decomposition of sisal, flax, and jute fibres, having lignin contents of 9.9, 2.0, and 11.8 %, respectively. They concluded that the lower lignin content in flax contributed to a higher decomposition temperature but resulted in a lower oxidation resistance, which would be provided by the aromatic structure of lignin [31].

Furthermore, there is another an important parameter is the fine structure of the fibre, it is also play a role in the flammability of the fibre [32, 33]. For cellulosic fibres in particular, higher levels of levoglucosan give higher levels of crystallinity during pyrolysis. A higher ignition temperature, however, also results from increased crystallinity as more energy is required to decompose the crystalline structure. For example, the activation energy of crystalline celluloses is about 200 kJ/mol whereas it is about 120 kJ/mol for amorphous cotton and ramie [33].

Increased orientation or degree of polymerization results in decreased pyrolysis. Basch and Lewin [32, 34] attributed the high thermal stability of ramie, when compared to cotton, to its very high orientation since the degree of polymerization and crystallinity of the two fibres are similar.

In addition, the higher the orientation, the lower the permeability of the fibre to oxygen [32]. A fibre with low crystallinity and a high degree of polymerization and orientation would, therefore, from a flammability aspect, be the best choice to use as reinforcement in a composite material.

10.1.4.1 Cotton Fibre

Cotton is a natural vegetable single elongated fibre, developed from an epidermal cell of the cotton seed, which grows in many countries of the world. The individual cotton fibres consist of a single long tubular cell. Its length is about 1,200–1,500 times than its width, where, its length is varies from 12 to 60 mm and a width of 15–24 μ depending upon its source [35].

The main producing countries of cotton fibre are the United States, Egypt and India. The highest quality cotton, which has very long and fine fibres, is growing in Egypt. It is generally recognized that, cotton is the most used textile fibre in textile industry. World textile fibre consumption in 1998 was approximately 45 million tons of this totals, cotton represented approximately 20 million tons [36]. Due to its versatile uses; most consumers prefer cotton personal care items to those containing synthetic fibre, where it has several attractive and useful properties, such as comfortable, soft hand, absorbent, good colour retention, machine washable and dry cleanable, good strength, well durability and easily sewing and handling (Fig. 10.4).

Distinctive Features Morphology of Cotton

As it is noticeable from the Fig. 10.5 [27], cotton fibre consists of primary and secondary layers, while lumen is present in the centre. Primary layer holds up to 30 % cellulose and non-cellulosic materials. This cellulose is of lower molecular weight with the degree of polymerization (DP) between 2,000 and 6,000. Secondary wall is rich in cellulose of higher weight with DP of 14,000 [38].

More detailed the cotton fibre has the following composition:

(a) Cellulose: 88–96 %, it is the main component of the cotton fibre and secondary wall possess highest percentage of the total cellulose.
(b) Pectin's: 0.9–1.2 %, these are made of ploygalacturonic acid, and its magnesium salts, methylester, xylose. They are present mainly in primary wall.
(c) Proteins: 1.1–1.9 %, these are made of protoplasm rest in lumen and aspartic, glutamic acid and praline. The primary wall contains 0.2–0.3 % nitrogen.
(d) Waxes: 0.3–1.00 %, they are composed of higher monovalent alcohol-tractional, palmitic, oleic acid, glycerine. Its melting point is 77 °C. They are found on surface of cotton and in primary wall.
(e) Organic acids: 0.5–1.00 %, these are salts of citric and L-maleic acid.
(f) Mineral salts: 0.7–1.6 %, these are hypochlorites, sulphates, phosphates, oxides of silicon, calcium, potassium, magnesium.
(g) Sugar: 0.3 % made of glucose, galactose, fructose and pentose.
(h) Toxine: 0.9 %, endotoxine, evolved from bacterial cells (0.017–100 g per bale of mass 218 kg).
(i) Vitamins and pigment (flavones compound).

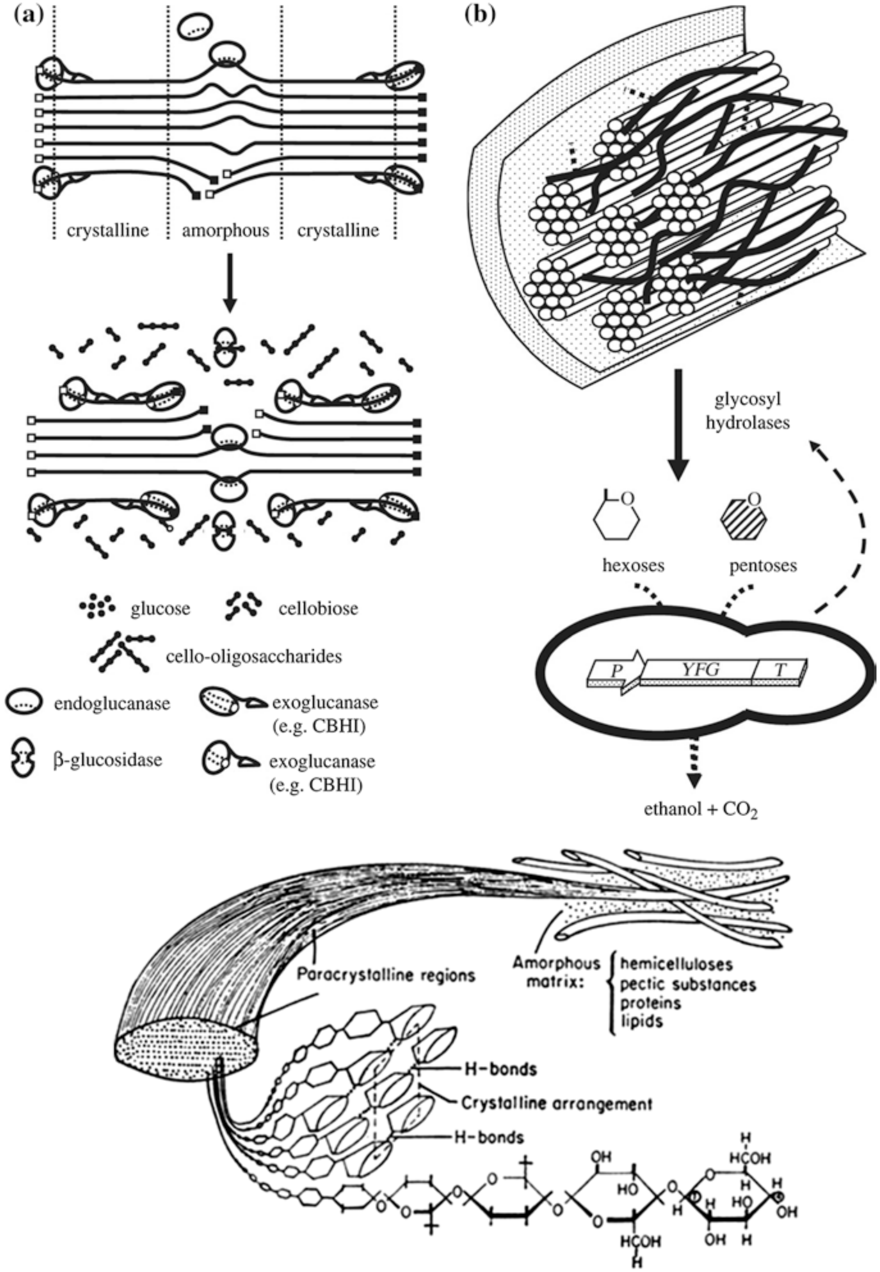
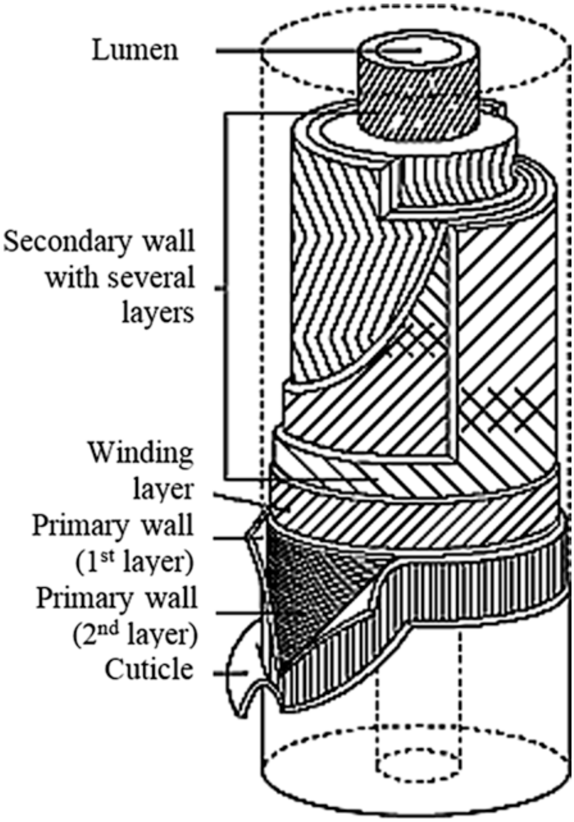


Fig. 10.4 Amorphous and crystalline regions of cellulose [37]

Fig. 10.5 Schematic structure of a mature cotton fibre, identifying its six parts [27]



10.1.4.2 Linen (Flax)

A flax fibre is a biodegradable natural composite material which exhibits good specific mechanical properties. Consequently, this fibre is foreseen as a reinforcement material in polymeric based structural composites in replacement of the largely used E-glass fibres. 1.2 tons of short flax fibres, 80 % of which is used in the textile industries and 20 % in composite materials, can be produced.

The multilayer composite structure of the flax fibre is presented in Fig. 10.6 [39]. The fibres are located within the stems, between the bark and the xylem. Around twenty bundles can be seen on the section of a stem and each bundle contains between ten and forty fibres linked together by a pectic middle lamella. Each fibre is made of a thin external layer, called the primary cell wall, and a thick secondary cell wall, which is divided into three layers.

The cell walls are made of cellulose microfibrils laid in spirals around the fibre axis and embedded in a pectic matrix. In the secondary cell wall, the angle between the microfibrils and the longitudinal axis (called the "microfibril angle") is about 10° [28, 40, 41]. In a flax bundle, the weight fraction of cellulose has been evaluated at 65–75 %, the one of non-cellulosic polymers (i.e.

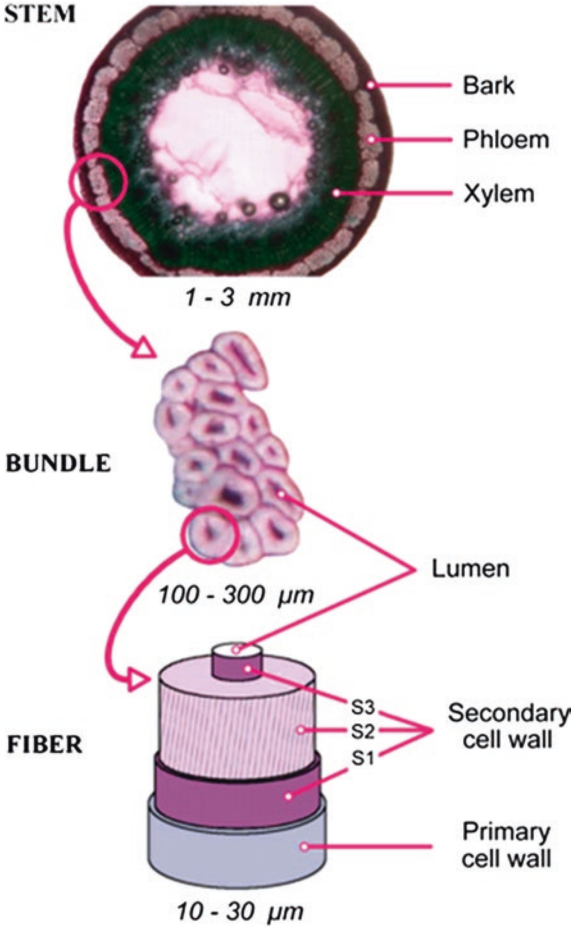


Fig. 10.6 Structure of flax: from the stem to the fibre [39]

pectins, hemicelluloses and lignin) at 20–25 % and the one of water at 8–10 %. Considering the microstructural arrangement, the cellulose microfibrils act as the reinforcement of the pectic matrix and the interface between these two materials is mainly composed of hemicelluloses [39, 42].

10.1.4.3 Jute

Jute is a natural biodegradable fibre with advantages such as high tensile strength, excellent thermal conductivity, coolness, ventilation function [43, 44]. Jute fibre is a bast fibre obtained from the bark of jute plant containing three main categories of chemical compounds namely cellulose (58–63 %), hemicellulose (20–24 %) and lignin (12–15 %), and some other small quantities of constituents like fats, pectin, aqueous extract. Jute fibre is composed of small units of cellulose surrounded and cemented together by lignin and hemi-cellulose [45, 46]. The low cellulose content, coarseness, stiffness, low extensibility, low grip performance.

A bast fibre used for sacking, burlap, and twine as a backing material for tufted carpets. Jute is one of the most affordable natural fibres and is second only to cotton in amount produced and variety of uses of vegetable fibres. Jute fibres are composed primarily of the plant materials cellulose (major component of plant fibre) and lignin (major components of wood fibre).

Chemical Composition of Jute Fibre

• Cellulose	65.2 %
• Hemi-cellulose	22.2 %
• Lignin	12.5 %
• Water soluble matter	1.50 %
• Fat and wax	0.60 %

Defects in Jute

Rooty Jute: in these jute the lower parts of jute fires contain barks.

Specky jute: this defects occur because of insufficient washing which causes the outer barks to adhere in some places.

Croppy Jute: this is a defect where the top end of the fibre become rough and hard. It is usually caused by careless steeping.

Knotty jute: the jute fibres contain knots in places and it is caused by insect bite or punctures.

Dezed or Dead fibres: due to over retting in moist condition, the fibre becomes dull, lose strength and becomes inferior for spinning.

Runners: this is a defect where long and hard barky ribbon of fibres remains in jute fibre.

Hunka: defects caused by non-removal of dried up base and hard bark from the fibres.

Mossy jute: fibres from short plants that cannot be properly stripped and cleaned contain broken piece of jute sticks etc.

Flabby or Fluffy jute: due to careless stripping, fibre loses firmness and becomes flabby and hairy.

Heart damage: These defects occur when jute fibre contains excess moisture when baled. The centre of the bale becomes badly tendered and in some cases fibres are reduced to powder.

10.1.4.4 Bamboo

Bamboo is a naturally occurring composite material which grows abundantly in most of the tropical countries. It is considered a composite material because it consists of cellulose fibres imbedded in a lignin matrix. Cellulose fibres are aligned along the length of the bamboo providing maximum tensile flexural strength and rigidity in that direction [47].

It has been used widely for household products and extended to industrial applications due to advances in processing technology and increased market demand. The chemistry of bamboo is important in determining its utilization potential. Several studies have investigated the chemical composition of bamboo. But systematic and thorough research on a commercially important bamboo species is needed to determine utilization potential for the products such as medium density fibreboard (MDF). Most of previous studies provide either only general information of several bamboo species or focuses on only one aspect of one species.

The chemical composition of bamboo is similar to that of wood. The main constituents of bamboo culms are cellulose, hemi-cellulose and lignin, which amount to over 90 % of the total mass. The minor constituents of bamboo are resins, tannins, waxes and inorganic salts. Compared with wood, however, bamboo has higher alkaline extractives, ash and silica contents [48].

Bamboo contains other organic composition in addition to cellulose and lignin. It contains about 2–6 % starch, 2 % deoxidized saccharide, 2–4 % fat, and 0.8–6 % protein. The carbohydrate content of bamboo plays an important role in its durability and service life. Durability of bamboo against mold, fungal and borers attack is strongly associated with its chemical composition. Bamboo is known to be susceptible to fungal and insect attack [49].

10.1.4.5 Hemp

Hemp is a natural, cellulosic and bast fibre. Hemp fibre is collected from the hemp plant. The plant from which hemp fibre is collected that is called Cannabis sativa. This plant is generally grows in the bank of Capsicum sea. It is interesting that this type of plant is growth naturally or in some reason it is cultivated manually. The cultivation process is near flax cultivation. It is a natural fibre and it has a chemical composition which helps us to identify this fibre from the others.

Hemp is a cellulosic natural fibre and cellulose is a main component of hemp fibre. The chemical composition of hemp fibre is presented as follow [50].

• Cellulose	77.77 %
• Hemicellulose	10 %
• Lignin	6.8 %
• Pectin	2.9 %
• Fat and wax	0.90 %
• Water soluble	1.73 %

10.1.4.6 Wood

Wood fibre are natural composite structures in which cellulose fibrils are held together by lignin and hemicellulose. The major constituents of wood fibre are lignin, cellulose, hemicellulose, and extractives. Each of these components contributes to fibre properties, which ultimately impact product properties.

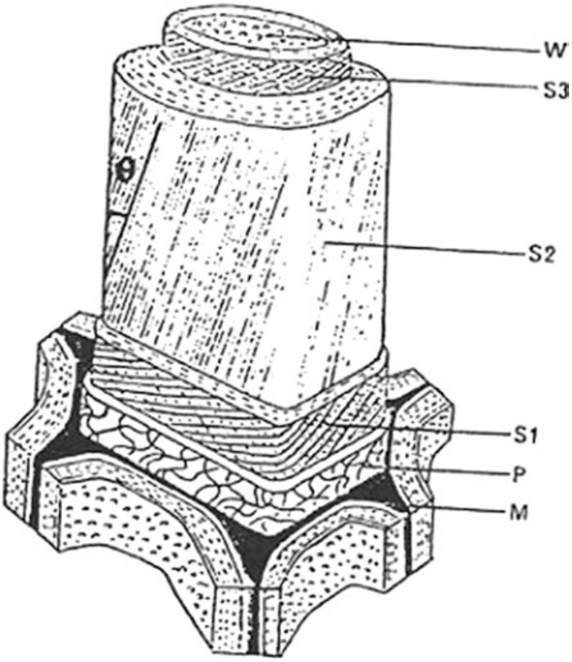


Fig. 10.7 Model for a pulpwood fibre. The middle lamella (*ML*), primary wall (*P*), outer (*S1*), middle (*S2*), and inner (*S3*) layers of the secondary wall, and the warty layer (*W*) are labeled accordingly

A model for wood structure of a typical softwood tracheid is described in Fig. 10.7. The middle lamella and primary cell wall of these fibres are often referred to as the compound middle lamella. The middle lamella contains a high proportion of amorphous material which holds neighbouring fibres together. The primary cell wall is approximately 0.03–1.0 μm thick, and also contains a high percentage of lignin. The secondary cell wall consists of three layers, labelled S1 through S3 from the outer to the inner layer. The S1 and S3 layers are thin, at 0.1–0.3 μm, while the middle layer (S2) is thick at 1–5 μm, and is said to be most responsible for the strength properties of individual fibres. The fibrils of secondary cell wall layers are wound helically around the fibre axis, while those of the primary wall are randomly oriented [51] .

Table 10.2 presents major chemical compositions of some wood species. Each of these components contributes to fibre properties, which ultimately impact product properties.

10.1.5 Regenerated Fibres

The first man-made fibres which were developed and produced used polymers of natural origin, more precisely of cellulose which is a raw material available in large quantities in the vegetable world.

Table 10.2 Chemical composition of some wood species [52]

Constituent (%)	Scots pine (Pinus sylvestris)	Spruce (Picea glauca)	Eucalyptus (Eucalyptus camaldulensis)	Silver birch (Betula verrucosa)
Cellulose	40	39.5	45.0	41.0
Hemicellulose				
-Glucomannan	16.0	17.2	3.10	2.30
-Glucuronoxylan	8.9	10.4	14.10	27.5
-Other polysaccharides	3.6	3.0	2.00	2.60
Lignin	27.7	27.5	31.30	22.0
Total extractives	3.5	2.1	2.80	3.00

Cellulose is the natural polymer that makes up the living cells of all vegetation. It is the material at the centre of the carbon cycle, and the most abundant and renewable biopolymer on the planet.

Cotton linters, wood pulp, viscose rayon, Cupra-ammonium, Cellulose Acetate (secondary and triacetate) and polynosic are High Wet Modulus (HWM).

- Cellulose is one of many polymers found in nature.
- Wood, paper, and cotton all contain cellulose. Cellulose is an excellent fibre.
- Cellulose is made of repeat units of the monomer glucose.
- The three types of regenerated cellulosic fibres are rayon, acetate and triacetate which are derived from the cell walls of short cotton fibres called linters.
- Paper for instance is almost pure cellulose.

10.1.5.1 Rayon (Viscose) Fibre

Originally, the word rayon was applied to any cellulose-based manufactured fibre, and therefore included the cellulose acetate fibres. However, the definition of rayon was clarified in 1951 and now includes textiles fibres and filaments composed of regenerated cellulose, excluding acetate. In Europe the fibres are now generally known as viscose, the term viscose rayon being used whenever confusion between the fibre and the cellulose xanthate solution (also called viscose—see below) is possible.

- Rayon is a manufactured regenerated cellulosic fibre
- It is the first manmade fibre
- It has a serrated round shape with smooth surface
- It loses 30–50 % of its strength when it is wet
- Rayon is produced from naturally occurring polymers and therefore it is not a synthetic fibre, but a manufactured regenerated cellulosic fibre
- The fibre is sold as artificial silk.

There are two principal varieties of rayon namely viscose and cupra ammonium rayon.

10.1.5.2 Cellulose Acetate

A manufactured fibre, in which, the fibre forming substance is cellulose acetate. Acetate is derived from cellulose by reacting purified cellulose from wood pulp with acetic acid and acetic anhydride in the presence of sulphuric acid.

The Acetate Fibre Characteristics

- Luxurious feel and appearance
- Wide range of colours and lustres
- Excellent drapability and softness
- Relatively fast drying
- Shrink, moth and mildew resistant
- Special dyes have been developed for acetate since it does not accept dyes ordinarily used for cotton and rayon.

Acetate fibres are the manufactured fibres in which the fibre-forming substance is cellulose acetate. The cellulose esters triacetate and acetate are formed through acetylation of cotton linters or wood pulp using acetic anhydride and an acid catalyst in acetic acid.

Acetate and triacetate fibres are very similar in appearance to the regular-tenacity viscose rayons. Acetates and triacetates are moderately stiff fibres and possess good resiliency on bending and deformation, particularly after heat treatment.

The abrasion resistance of acetate and triacetate is poor, and these fibres cannot be used in applications requiring high resistance to rubbing and abrasion; however, the resistance of these fibres to pilling is excellent. While acetate and triacetate are moderately absorbent, their absorbencies cannot compare with the pure cellulosic fibres. The hand of acetate fabrics is somewhat softer and more pliable than triacetate, which possesses a crisp firm hand. Fabrics of both fibres possess excellent draping characteristics. Fabrics of acetate and triacetate have a pleasing appearance and a high degree of lustre, but the lustre of these fabrics can be modified through addition of delusterants.

Both acetate and triacetate are susceptible to attack by a number of household chemicals. Acetate and triacetate are attacked by strong acids and bases and by oxidizing bleaches. Acetate has only fair sunlight resistance, whereas the sunlight resistance of triacetate is superior. Both fibres have good heat resistance below their melting points.

Acetate and triacetate cannot be dyed by dyes used for cellulosic fibres. These fibres can be satisfactorily dyed with disperse dyes at moderate to high temperatures to give even, bright shades. Acetate and triacetate dry quickly and may be tumbling dried or drip-dried.

10.2 Fire and Flame Retardancy Finishing of Cellulosic Materials

The flame retardant treatment is one of the oldest forms of textile finishing; hazards associated with ready combustibility of cellulosic materials were recognized as early as the 4th century Bc [53]. The concept of protecting textiles from burning dates back to 1821 in France when Gay Laussac treated hemp, jute and linen fabric with a mixture of ammonium phosphate, ammonium chloride and borax. The first successful, launder-resistant, flame retardant finish for fabric was based on the work of Perkin who precipitated stannic oxide within the fibre. This fabric was flame resistant but after glow was severe and persistent enough to completely consume the fabric [54].

10.2.1 Uses of Flame Retardant Fabrics

Flame retardant fabrics are needed for a variety of uses such as for [55]:

1. Apparels and garments, sleepwear, nightwear, children's wear, loose garments, sarees, shawls, kitchen wear, etc., where there are chances of accidental contact with flame.
2. Uniforms for fire—fighting personnel.
3. Dresses, boiler suits and protective clothing for work men in many industries like petroleum and petrochemicals, oils, paints and varnishes, mining, iron and steel, explosives, matches, organic chemicals and solvents, electricity generation and distribution, foundry, welding, petrol and diesel pumps, cooking gas storage and distribution etc.
4. Home furnishing and decorations—curtains, drapes, upholstery, bedding, mattresses, wall coverings and trimmings etc.
5. Carpets and rugs.
6. Industrial fabrics-Brattice cloth for coal mines, carpet backing fabrics, barrier fabrics as overlay on foam and rubber cushions, underlay in motor vehicles, wall coverings, decorative fabrics etc.
7. Hotels, restaurants, clubs, rest houses, dormitories, auditoriums, theatres, cinema halls, religious worship and congregation halls, marriage halls, hospitals, schools, colleges etc.
8. Armed forces (Defence)-clothing for airmen and fire fighting crew, overalls, parachutes, awning, tarpaulins, canvas including skop (support kit overhead protection), claddings and shelters, etc. also for paramilitary, police etc.
9. Exports-garments, curtains, wall coverings, bad covers, mattresses, quilts, airline furnishings, automobiles fabrics.

In addition to satisfying obligatory fire requirements and regulations, an efficient fire retardant has to have the following features: [56–58]

- It must have thermal stability at the usual polymer processing temperature
- The retardant should have compatibility with the polymer and no leaching should occur
- The additive has to conserve its fire retardant properties when exposed to fire action
- The retardant has to decrease the creation of toxic gases and smoke during combustion
- The amount of required additive to achieve flame retardancy should be at a low level [usually not more than 10 % wfw] to reduce costs and its effect on the mechanical properties of the material
- The retardant has to be easy to introduce into the polymer mass
- The retardant has to be easily removed from the polymer during recycling
- The additive must have no harmful environmental properties nor be harmful to health
- The additive should be commercially available and cost efficient
- The retardant must not provoke corrosion.

10.2.2 Flame Retardant Cellulosic Fabric

Cellulosic fabrics have low fire resistance [55]. They are composed of carbon and hydrogen (fuels) and oxygen (supporter or combustion) and burn very easily. The burning process of cellulosic materials is an oxidation process. This process may be accompanied by a flame or glow; most organic fibres undergo a glowing action after the flame has been extinguished. The glow may cause much damage as the flaming itself, since it can completely consume a textile. Flaming and glowing are distinctly different processes, taking place at different temperatures [54]. It is useful, however to define a number of terms before going into details of fire and flame retardant finishing of textile.

10.2.2.1 Fire-Proof Textile

This term is applied to textiles, which are essentially unaffected fire. This means that they do not support fire (flame or glow) and that there is little or no chemical or physical change when the textile is exposed to flames. Few textiles fall in this category. Carbon, asbestos, basalt and glass fibres are the one in common use today [54, 55, 59].

10.2.2.2 Flame Resistant Textile

Fabric that will not support a flame after the source of ignition has been removed is said to be flame resistance. A flame resistance fabric may continue to burn by the glow mechanism although a flame does not exist. Flame resistant fabrics can also char or melt [54, 60].

10.2.2.3 A Glow Resistant Textile

Fabric will not continue to burn by the glow mechanisms once the source of ignition has been removed. Glow-resistant textile may char or melt [55, 60].

10.2.2.4 Fire Resistant Textile

Fabric is not only flame resistant but also glow resistant. Thus, flaming and glowing cease once source of ignition has been removed. There will be a change in the physical and chemical characteristics, the textile may char or melt [55, 60].

10.2.3 Theory of Combustion

When solid materials are heated, physical and chemical changes occur at specific temperature depending on the chemical make-up of the solid. Thermoplastic polymers soften at the glass transition temperature (Tg), and subsequently melt (Tm) at some higher temperature (Tp), both thermoplastic and non-thermoplastic solids will chemically decompose (pyrolysis) into lower molecular weight fragments. Chemical change begins at (Tp) and continues through the temperature at which combustion occurs (Tc). These four temperatures are very important when considering the flame resistance of fibres. Another important factor in combustion is the limiting oxygen index (LOI). This is the amount of oxygen in the fuel mix needed to support combustion. The higher the number, the more difficult it is for combustion to occur. For non-thermoplastic fibres, (Tp) and or (Tc) are less than (Tg) and/or (Tm), however for thermoplastic fibres (Tp) and/or (Tc) is greater than (Tg) and or (Tm). Natural fibres are not thermoplastic, therefore when they are subjected to a heat source, pyrolysis and combustion temperatures are encountered before softening or melting temperatures are reached and eventually ignite. On other hand, low melting thermoplastic fibres will melt and drip away from the flame before pyrolysis and combustion temperature is reached. However if the melt doesn't shrink away from the flame front, pyrolysis and combustion temperatures are eventually reached and ignition will occur [61, 62].

Natural fibres can be made flame retardant and like some synthetic fibres, nomex, Kevlar and PBI, offer protection to a wearer because they do not shrink away from a flame. Thermoplastic fibres may appear to offer protection because they pass the ignition test by shrinking away from the flame, however, in reality this exposes to wearer to direct heat and burns caused by contact of the molten mass with the body [62, 63].

10.2.3.1 Combustion or Burning Process in Textile

Combustion is defined as fast, self-accelerating exothermal redox process that is able to spread in the environment and accompanied by luminosity and the formation of flame [61, 64].

Combustion is a chain reaction that may be initiated and propagated by free radicals like the hydroxyl free radical. Hydroxyl radicals may be produced by the reaction of oxygen with macro alkyl radicals. Halogen radicals produced by the reaction of hydroxyl radicals with halides such as HX, may serve as terminators for the chain reaction [61] (Fig. 10.8).

Combustion is usually a gas phase phenomenon. Volatile combustible species oxidize exothermically in the gas phase. Afterglow or glowing combustion is a form of non-gas phase combustion. Here the substrate is oxidized in the condensed phase to form both solid and gaseous products. This usually takes place at temperatures well below the ignition temperature of the material. For instance, the carbon residue in a carbon rich material is oxidized in the solid phase.

Emman's fire triangle is generally used to illustrate how combustion works and is shown in Fig. 10.9 [65]. For a sustained fire, three elements are needed [66]:

- Fuel—Volatile combustibles from carbon rich substance thermally degrading
- Heat—Supplied by the exothermic oxidative destruction of fuel
- Oxidizing agent—Oxygen provided by air

In the case of polymers, an external heat source is needed to ignite the substrate. The heat, to which the material is exposed, causes the high molecular weight

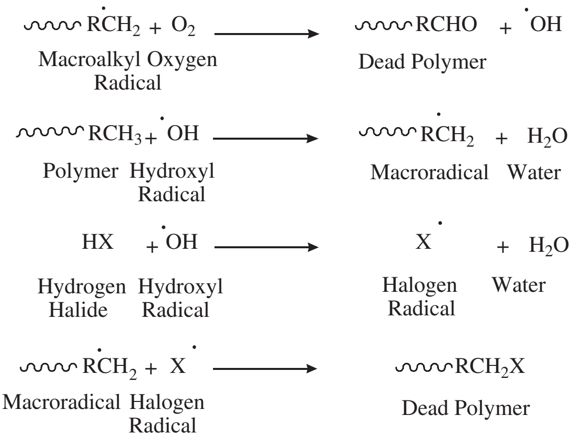


Fig. 10.8 Combustion exothermal redox process

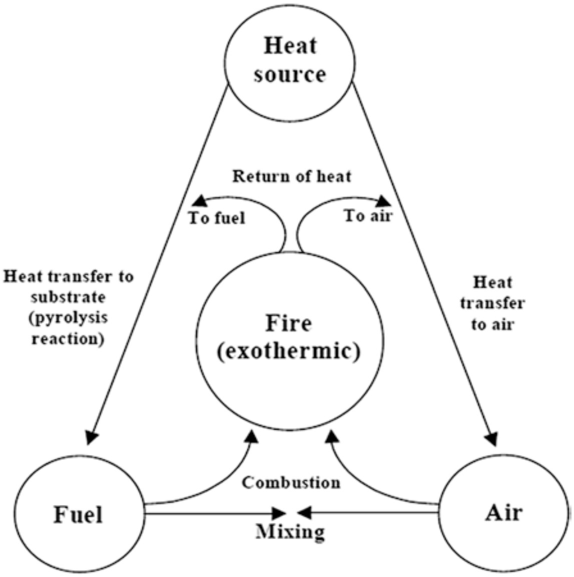


Fig. 10.9 Emman's fire triangle

polymer to thermally decompose [67]. On thermal decomposition, the polymer releases smaller volatile compounds that act as fuel to the fire. These combustible species mix with the oxygen in the air to form an ignitable mixture. Exothermic oxidation of the volatiles occurs and the material burns. Light and more heat are generated. The process becomes self-sustaining and functions with a feedback loop as can be seen in the fire triangle (Fig. 10.9).

The product of the fire differs for each combustible compound. In the case of polymers, the gases produced by combustion tend to be mainly carbon dioxide (CO_2), carbon monoxide (CO) and water vapour (H_2O). The solid residue is mostly carbon (C) and ash (oxidised metals) [65, 66].

A flame retardant system is a compound or compositions added to materials, which increases a given material's resistance to combustion. The flame retardant system can either be added to the polymer during the polymers manufacturing step, during master batching of the polymer additives or during the production of the plastic artefacts.

An effective name retardant needs to hinder the supply of one or more of the elements required for sustained combustion [66]. The objective of flame retardants is to lower a polymers inherent fire risk by lowering the rates of combustion and flame spreading under fire conditions [68]. The use of flame retardants may prevent a small fire from becoming a major catastrophe [69]. In order for a flame retardant to be effective, it must interact and interfere with the degradation of the host polymer at the polymer's degradation temperature [70]. The degradation temperatures for the most widely used polymers are between 200 and 400 °C [71]. Increased fire resistance can be achieved through several mechanisms, as can be seen in Fig. 10.10 [72]. The interference with the combustion process may take place in the gas or vapour (flame zone) or condensed or solid phases (polymer melt).

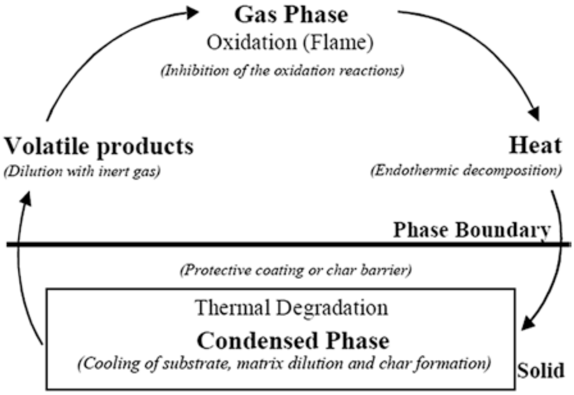


Fig. 10.10 A simplified model for combustion and flame retardancy

A flame retardant is not designed to prevent the material from igniting, but to keep the flame spread rate to a minimum and prevent sustained burning. Flame retardants tend to retard the spread of flames by increasing the given polymer's resistance to ignition. Ignition is unavoidable, because most substances will flame up if subjected to high enough levels of fire stress—thermal radiation [66].

A useful and complete description of the mechanisms of general retardant systems is provided in the review articles of Green [69, 73]. Different flame retardant systems can be identified, all of which function by different mechanisms. Flame retardants interfere with the thermal decomposition pathway of the polymeric material. Different compositions interact differently with different polymers and a flame retardants use is thus very specific to the particular substrate for which it was designed.

Some flame retardants which form acids during combustion—like the halogens operate through gas-phase free-radical inhibition. Other groups of retardants produce many non-combustible gases and dilute the amount of fuel or oxygen supplied to the fire. The formation of solid residues on the surface of the burning material is another way of reducing flame spread. Some reduce the rate of heat release during combustion by affecting the heat transfer pathway to the polymer substrate. Another group of flame retardants form a foaming char on the surface of the combusting material. These additives are called intumescent systems. A system can also operate through combinations of the above-mentioned mechanisms [69].

The following terms and definitions are used to describe the different mechanisms by which flame-retardants operate [74]:

- *Inert gas dilution*: Large quantities of inert and *non-combustible* gasses are produced on thermal decomposition of the additive. The concentration of oxygen and combustible species are reduced and the fire dies.
- *Thermal quenching*: The surface temperature of the polymer is reduced or kept low by the *endothermic* degradation of the additive. Due to the lower substrate temperature, less combustible products are produced and the thennal degradation is retarded.

- *Physical dilution*: Large quantities of inorganic fillers (such as glass fibre) are added to the polymer matrix. The amount of flamable material (polymer) is thus reduced and the substrates fire resistance increased.
- *Chemical interaction*: Some flame retardants thermally dissociates into radical species that then interferes with the gasphase combustion of the combustibles.
- *Protective char*: On thermal decomposition, the additive forms an insulating char barrier on the surface of the polymer. This char reduces heat transfer for to the polymer, diffusion of oxygen to the area of decomposition and diffusion of combustibles to the flame zone, retarding the combustion.

An ideal flame retardant will have the following properties: [65, 66, 69, 73, 75]

- It reduces flammability to the required standard
- It is thermally stable at the processing temperatures
- Have long term compatibility with the polymer matrix (i,e, does not “bloom”)
- Maintains or improves the mechanical properties of the polymer
- Represents no health hazard; and
- Is cost effective.

The flame retardant must not decompose at temperatures below the processing temperatures of the polymer. Ideally, the flame retardants decomposition temperature should be several degrees higher than the polymer processing temperature.

Large-molecule flame-retardants in the form of polymeric and oligomeric compounds are gaining ground in the industry because they are more resistant to blooming and leach out and promise greater compatibility with host plastics than traditional flame retardant additives [76].

Figure 10.11 shows the mechanism of burning of polymers. The endothermic Step 1 produces low molecular weight pyrolysis products that combine with oxygen in exothermic Step 2 gas phase reaction to produce oxidation products. The heat generated in this step goes back (Step 3) to polymer to continue its decomposition.

Any compound or method inhibiting one or more steps in this burning process is potential flame retardant [62, 77].

Figure 10.11 shows the consecutive reactions during burning. When a solid fibre is ignited two successive chemical processes decomposition and combustion take place and these processes are linked together via a thermal fed bake. The

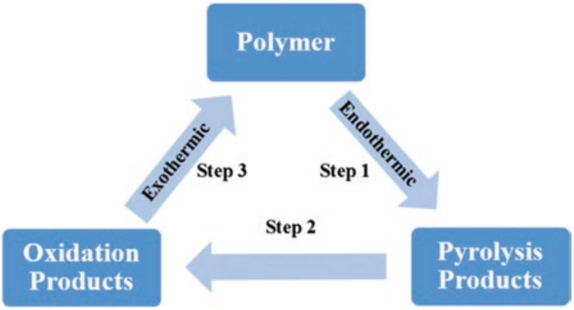


Fig. 10.11 Polymers burning mechanism

pyrolysis Step 1 required heat (Q1), while combustion Step 2 generated heat (Q2). The contact area of ignition (A) is also important. A high value of (Q1) and low values of (Q2) and (A) would lead to flame resistance [62, 77].

10.2.3.2 Mechanism of Fire and Flame Retardant

Burning of Cellulose

In the development of better flame retardants it is helpful to know what chemical reaction occur when cellulose burns and how the reaction are affected when fabrics are treated with a flame retardant. The burning characteristics of cellulose depend to a considerable extent on the chemical and thermal properties of the anhydroglucose units, on the availability of oxygen, and on the nature of non-cellulosic materials that may also be present. Fibre properties such as the ignition temperature, the rate and heat of combustion products, and moisture content also affect the burning characteristic of cellulose [59, 62, 77].

Cotton is a combustible material. Presence of oxygen and a high temperature (360–420 °C) can initiated combustion of cotton which can be either burning (flaming combustion) or smoldering (smolder combustion). The intrinsic ignition time, on index of auto ignition, for cotton at 500 °C is 15.6 s, which comes down at 600 °C to 6.7 s and further at 700 °C to only 3.1 s. Cotton has an ignition temperature of 400 °C and burns readily to attain a maximum temperature of 860 °C char formation and after glow. The sequence of steps in the combustion of cotton is ignition; propagation and afterglow temperature within burning cellulose are reported at 413 °C during flaming and 600 °C during after glow. Ignition is controlled by various factors such as heat transfer from the source of ignition to cotton, thermal decomposition of cotton and reactions of decomposition products with the environmental oxygen. Thermal decomposition of cotton release a large number of combustible gases which can sustain ignition at and above certain concentration levels with oxygen of the air. A burning fabric generating more heat requires less ignition energy to continue its burning [77]. So, the effect of heat on cellulose is varying important, it makes property changes. The rapid reaction of degree of polymerization has already been noted, and it has been suggested [78] that the chain breaks occur at strain points at the crystalline-amorphous boundaries. The number of hydroxyl groups decrease while carboxyl group increase [79]. Even very short heating times decrease the accessibility of cellulose to H_2O and dye molecules and strongly increase its rate of acid hydrolysis. An increase in the crystalline lattice spacing has been shown while the chain orientation is reported to be unaffected [80].

It has found that there are two decomposition reaction occurred by controlled temperature. In the first reaction, which occurs between 200 and 280 °C water is lost and anhydrocellulose is formed [60].

$$(C_6H_{10}O_5)_n \xrightarrow[200-280\ ^\circ C]{\text{Heat}} n\ 1,2\text{-anhydrocellulose}$$

$$+\ nH_2O \xrightarrow{\text{Heat}} \text{Char} + H_2O + CO + CO_2$$

This anhydrocellulose decomposes further at elevated temperature to various volatile products such as alcohols, aldehydes and alkanes, flammable gases, carbon monoxide, ethylene, methane and non-flammable gases, carbon dioxide, water vapour and char.

The second reaction, involving thermal scission of glucosidic linkages and levoglucosan formation predominates at temperature above 280 °C.

$$1,2\text{-anhydrocellulose} \xrightarrow[200-340\ ^\circ\text{C}]{\text{Heat}} 1,6\text{-anhydrocellulose (Levoglocosan)}$$

$$1,6\text{-anhydrocellulose} \xrightarrow{\text{Heat}} \text{Char} + \text{Gases} + \text{Liquids} + \text{Tar}$$

Gases: combustible (methane, ethane, carbon monoxide) and non—combustible (formaldehyde, carbon dioxide etc.)

Liquids: Water, Alcohols, Aldehydes, Ketones, Organic acids. [80]

$$\text{Liquids} \xrightarrow{\text{Heat}} \text{Gases} + \text{Tar}$$

$$\text{Tar} \xrightarrow{\text{Heat}} \text{Gases} + \text{Liquids} + \text{Char}$$

Levoglucosan is the major product formed by the pyrolysis of cellulose it is the cyclic created when the β-1,4-glucosidic linkage is split, and a molecule of water is lost between the C(1) and C(6) hydroxyls of the anhydroglucose.

The burning of cellulose (Fig. 10.12) takes place in two ways: flaming and glowing both processes originate from either an open flame or a hot surface (above 300 °C). In the flaming process the thermal decomposition of cellulose results in gaseous, liquid, tarry and solid products [81–88].

The competition between volatile and char formation confirms a three-stage process which depends on both temperature and the exact nature of the flame retardant present [82]. Figure 10.13 shows the overall scheme, which builds on previously published mechanisms [22, 89].

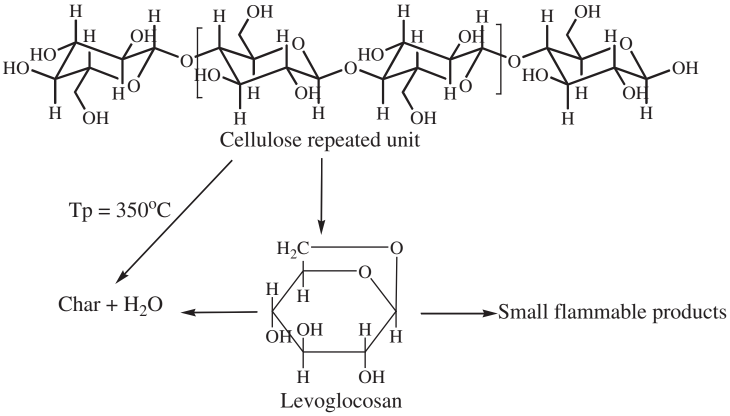


Fig. 10.12 Cellulose pyrolysis products

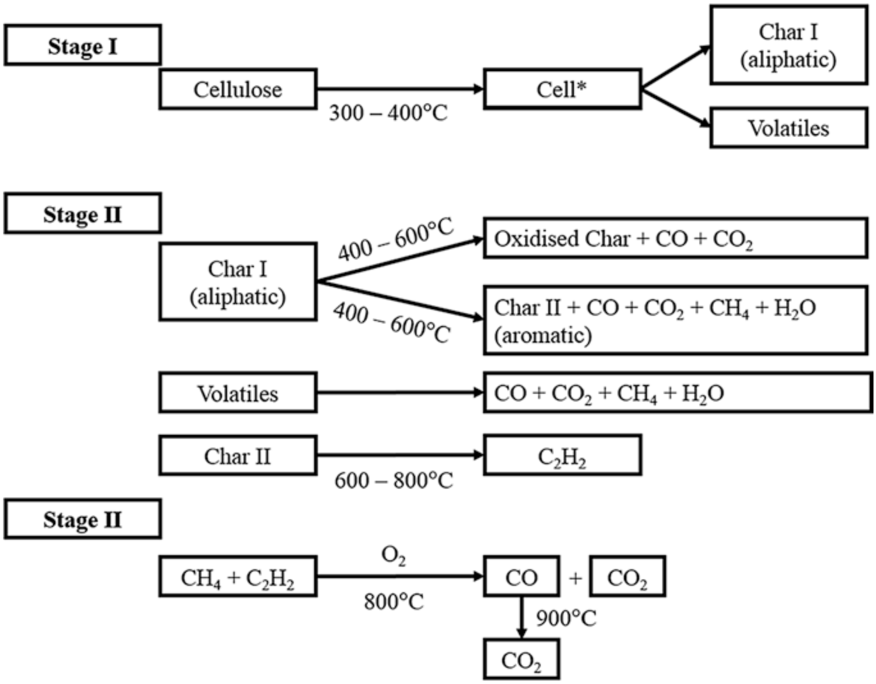


Fig. 10.13 Pyrolysis of cellulose and char formation

Stage I: shows the well-established competing mechanisms of char formation and volatilisation within the temperature range 300–400 °C

Stage II: within the range 400–600 °C, shows a competition between char oxidation and conversion of aliphatic char to an aromatic form. Volatiles from Stage I are also oxidised within this range to yield similar products to those formed from char oxidation and aromatisation.

Stage III: During the higher temperature regime of 600–800 °C, some char decomposition to acetylene occurs, while above 800 °C, this stage follows during which complete combustion of all remaining carbonaceous species to CO and CO_2 takes place.

As the flammable gases burn, the liquids are volatilize, and some of these volatile fractions burn, where as other portions give a carbonized residue that does not readily burn. This process continues until only carbonaceous, begins. The residual carbonaceous matter glows, oxidizes, and continuous to glow until essentially all organic matter is consumed and only a fluffy ash is left. At flaming cellulose temperature degradation of cellulose precedes first the formation of levoglucosan by scission of the (1–4) glucosidic linkages of cellulose and subsequently by intermolecular rearrangement of the fragments [62, 81–85]. The levoglocosan is thought to undergo dehydration and polymerization to form char.

The rate controlling reaction in the thermal decomposition of cellulose involves the formation of levoglocosan, chemically 1,6-anhydroglucopyranose. Levoglucosan remains a major pyrolysis product in air pyrolysis.

Levoglucosan yields are strongly influenced by even traces of impurities present in or added to the cellulose. It has been shown that acidic impurities can either increase or decrease the percentage of levoglucosan in the tar, depending on their concentration; while basic impurities depress levoglucosan formation at all levels [84, 85].

Flammability of the cellulose seems to vary, within narrow limits, with levoglucosan formation. These factors explain the observed increase in flammability of cellulosic textile.

When treated with low concentration of flame-retardants. The continued flammability of cellulose in the presence of sufficient flame retardant to depress or eliminate levoglucosan is attributed to formation of other volatile compounds [80].

Crosslinking with formaldehyde influences both levoglucosan yields and flammability [88]. The levoglucosan content decreases with increase in amount of formaldehyde reacted with cotton. This decrease is explained by the lower tendency of the crystalline faces with substituted C2 and C6 to undergo the unzipping reaction [80–85]. It is possible that the crosslinks bring about an additional pyrolysis path, different from that leading to levoglucosan and necessitating higher activation energy. In the case of rayon, the levoglucosan yield increases with the extent of crosslinking [85].

Burning of Flame-Resistant Cellulose

There are a number of theories proposed and postulated to achieve flame retardant properties and explain the function of them in cellulosic fabrics with the aid of additives. Such an additive, to be a successful player in this field, might take one or more of following roles and categories [62, 90]. It must inhibit one or more steps of the burning process—ignition, propagation and afterglow. It must either dissipate heat internally or conduct the heat away from the flame front like a “heat sink”—thermal theory.

It must form a glassy film of molten material at the fabric surface, which will acts as a shield between the fabric and oxygen thereby terminating flame propagation—Coating theory. It must dilute the flammable gases or blanket the substrate with a so—called atmosphere—gas theory. It, being a Lewis acid or base or their precursor, catalyses dehydration mechanism at the flaming temperature—Chemical theory.

Coating Theory

According to the coating theory, an effective compound forms a glassy skin and stable foam on the fibre surface. Such a flame retardant coating protects the fabric from the air by serving as a barrier to the flame and by entrapping the volatile tars evolved during combustion [59, 90].

Gas Theory

The gas theory states that the flame retardant decomposes at burning temperatures to give gases which do not burn but which will dilute the flammable gases produced by the decomposition of the cellulose to a concentration below which they can ignite and burn [59].

Thermal Theory

Two thermal mechanisms have been proposed for the retardation of the burning of cellulose. The first one is proposed that the caloric input from a source is dissipated by an endothermic change of retardant, such as fusion and sublimation of the flame proof. Such endotherms prevent propagation of the flame. The second mechanism is proposed that the heat supplied from the source is conducted away from the fibres so rapidly that the fabric never reaches combustion temperature [59].

Hydrogen Bonding Theory

It has been suggested that a majority of flame retardant are strong hydrogen bonding agents. Therefore, when water (the bridging medium between cellulose hydroxyl groups), is lose at higher temperatures, the bridges may be maintained by the strong hydrogen bonding activity of the flame retardant, thus stabilizing cellulosic fragment by reducing their volatility and hence, their combustibility. Although this mechanism may be a factor, it seems weak. It is improbable that such bonds could continue to exist at 400–500 °C [59, 85].

Catalytic Dehydration of Cellulose to Carbon and Water

Ideally flame retardant would direct the decomposition of cellulose into carbon and water. Theoretically this can be accomplished through dehydration reactions, and several dehydrating compounds are known to be good flame retardants for cellulosic fibres. Basically, the path of decomposition is altered, so that the amount of flammable gases and tars so reduced that combustion will not continue once the source of flame is removed [59]. The most recent and widely accepted modification of the theory states that flame retardancy is brought about by the catalytic dehydration of the cellulose through the reaction of Lewis acid with the cellulose via a carbonium ion mechanism. The flame retardant (Lewis acid) may be either present or produced from its precursor at a temperature close to that of burning cellulose [84].

In considering the dehydration theory, two types of burning will be considered flaming and glowing. The tar from flame resistant cellulosic fibres contains little or no levoglucosan, whereas that from untreated cellulose contains levoglucosan as a major component. The higher the ratio of carbon monoxide to carbon dioxide or the ratio of chars to tar, the better the flame resistance [81, 83].

Parks et al. [91] suggested that prevention of formation of levoglucosan, the major component of tar from untreated cellulose, or altering the path of decomposition to yield more char would result in flame resistance.

The prevention of formation of levoglucosan alone appears to impart flame resistance. It seems that formation of large percentage of carbon is much more important for fire resistance than lack of levoglucosan formation. Lack of levoglucosan in the decomposition product is important in that it can influence the amount of carbon resulting from dehydration reaction [81, 85].

Chemical Theory

Effective chemical retardants may be considered to act in either the solid or vapour phase, or a combination of the two. Retardants, which act in the gas phase, exert their effect by functioning as free radical [90].

$$\begin{gathered} R-X+P{-}H \rightarrow H-X+R-P \\ H-X+H^{\bullet} \rightarrow H_2+X^{\bullet} \\ H-X+OH^{\bullet} \rightarrow H_2O+X^{\bullet} \end{gathered}$$

Inhibitors, which slow the oxidation processes, and decrease the heat retardant to the polymer surface. Those retardants, which act in the condensed phase, may operate by inhibiting the decomposition of cellulose so that the chain does not break down to form flammable gases, or much more commonly, they act to alter rather than inhibit the degradation reaction. The mode of decomposition is changed to favour the formation of non-volatile residue rather than flammable gases [61].

Mechanism of Retardant Action on Cellulosic Materials

Cellulose flame retardant may operate through one of two basic mechanisms, solid phase (condensed phase) or vapor phase flame retardant.

Halogens are known to be efficient flame retardant agents for cellulose and other polymers [92] and act mainly in vapor phase via free radical inhibition.

However, this radically couples with free radicals produced in the combustion process and terminates the reaction.

A numerous investigator has characterized the effect of which solid (condensed) phase active flame-retardant exerts on cellulose [75, 93, 94]. Figure 10.14 illustrate the depolymerisation of cellulose.

The more effective flame-retardant finishes for cotton have based on organophosphorus compounds. These phosphorus compounds are relatively expensive, compared to many other types of organic compounds and contribute greatly to the high cost of flame retardant. Substitution of low cost nitrogen compounds for the phosphorus component in the flame retardants is one method of reducing cost. The use of nitrogen compounds was recognized many years ago when melamine and urea resins where incorporated into flame retardants systems based on chlorinated paraffin [60, 95].

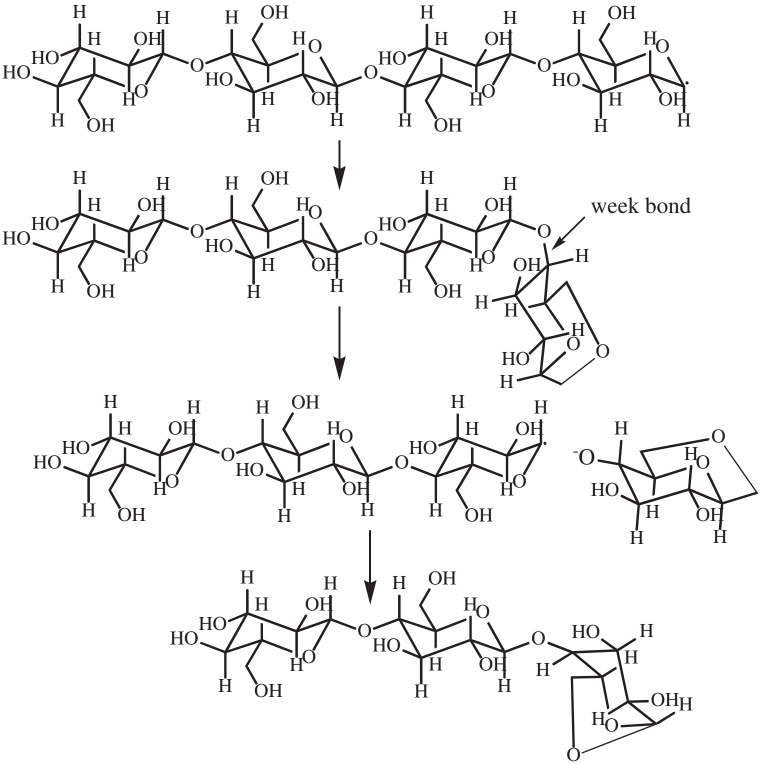


Fig. 10.14 Proposed depolymerization of cellulose

Pyrolysis of brominated wood was examined in detail by chemical, spectroscopic, and thermal analysis and determined the effect of bromine upon the cellulose and the distribution of the bromine in the products of pyrolysis [55].

A numerous investigators have characterized the effect of which solid (condensed) phase active flame-retardants exerts on cellulose [93, 94]. Their results are consistent in showing that reduction in tar formation, coupled with increased char yield, are the most important effect of the retardant action.

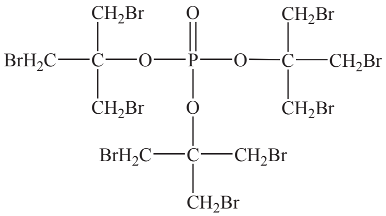
The reaction of thermal degradation of the cellulose (pyrolysis) is primarily unzipping depolymerization, which produces levoglucosan and secondary products, almost all of which are volatile and flammable. The reactions of the other set appear to have much lower energies of activation and proceeds at essentially the same moderately slow rate at all pyrolysis temperatures. These reactions lead mainly to nonvolatile char and nonflammable gases, such as water and carbon dioxide. Obviously then, condensed phase flame retardant action on cellulose could results from the catalysis of the latter reaction set and/or inhibition of the former.

Flame retardant based on phosphorus, sulfur, boron, and other acidic forming materials act via dehydration to produce water and char at expense of flammable tars. Most commercial treatments for cellulose are based on phosphorus, and consequently the effect of the structure of phosphorus based materials on the mechanism and efficiency of flame retardancy has been widely studied. Acidic phosphates act via phosphorlation, presumably at the C-6 hydroxyl of the anhydroglucose unit [64]. Consequently, increases of esterification are likely to be more efficient in promoting flame retardancy.

10.2.4 Phosphorous Flame Retardant Synergism

10.2.4.1 Halogen—Phosphorus Synergism

Halogen phosphorous synergism is often confused by analogy with the strong and well established halogen antimony synergism. Unlike antimony halogen synergism, phosphorous halogen synergism is not general. The postulated formation of phosphorous oxyhalides completely lacks experimental support. However, good additive results are often obtained with combinations of halogen- and phosphorous-based flame retardants [96]. An instance of bromine and phosphorous synergism is found in the structure of the following brominated phosphate ester:



10.2.4.2 Antimony—Phosphorus Synergism

There are a number of published formulations showing the attempted use of antimony oxide in combination with phosphorous and halogen flame-retardants. Results sometimes appear favourable, but quantitative studies show convincing evidence of an antagonism between antimony and phosphorous. In the most severe case, the one element cancels out the effect from the other, and in other cases, the effect is less than an additive. A detailed study of triaryl phosphate and antimony oxide in polyvinyl chloride (PVC) showed that this antagonism only occurred in a part of the composition range. The antagonistic effect probably is the result of the formation of antimony phosphates that are very stable and practically inert fillers [96].

10.2.4.3 Nitrogen—Phosphorus Synergism

As with many other multi-component products, flame retardant systems are regularly produced by simply mixing two or more ingredients together. The efficiency of flame retardants can be greatly influenced by synergy between the formulation components [96]. The properties of the final product or system depend on the proportion of the individual components used. Synergy is the phenomenon when a compound formulation (a combination of two or more components) leads to a desirable property that is better than the property obtained with the ratio of the individual compounds. However, such component combinations can unfortunately also lead to undesirable effects. A reduction in the desirable property due to the combination is called antagonism. Figure 10.15 shows possible responses for a two-component system [97].

Compounds containing nitrogen and phosphorus have been used for a long time as fire retardant for example (phosphoric acid/urea, tetrakis hydroxymethyl phosphonium chloride (THPC)/ammonia, urea or trimethylol melamine). It was established that incorporation of N—containing compounds in the finishing formulation with p—containing compounds increase the flame retardancy properties of the finished fabrics [90, 98].

In most of the above cases, the role of nitrogen was believed to influence the attachment of phosphorus to the cellulosic fabric [99].

It has reported that cellulose derivatives containing phosphorus are very much prone to dehydration reaction resulting in formation of char. A synergism

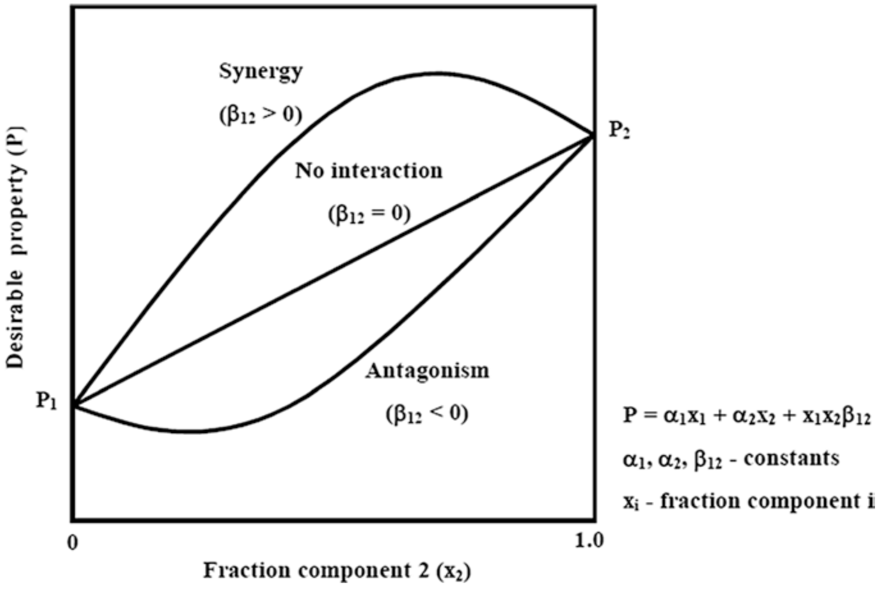


Fig. 10.15 The property (*P*) evaluation of a two component system blend

enhancement in the efficiency of phosphorus—based flame retardants by compounds containing nitrogen atoms has been well documented. However, it is noteworthy that not all N-containing compounds are effective but only those containing nucleophilic nitrogen atoms, e.g. amines and amides are useful adjuncts [100].

Incorporation of a nitrogenous component to phosphorous—containing compounds has the advantage of minimizing acid degradation of cellulose by releasing phosphoric acid and also enhancing flame retardation [101].

Using the nitrogen compounds have many advantages, low toxicity, their solid state and in case of fire, the absence of dioxin and halogen acids as well as their low evolution of smoke. Their efficiency lies between that of halogen compounds and that of aluminium trihydrate and magnesium hydroxide. The metallic hydroxides split off water and are environmentally friendly, but their low activity requires high concentration which changes the mechanical properties of the matrix that they are applied to. Flame-retardants based on nitrogen are environmentally friendly because they do not add any new element to those already present in the polymers. The final and best argument is their moderate price [99]. Using a comparable level of flame retardant could be achieved using a smaller add—on of phosphorus/nitrogen mixture than with phosphorous or nitrogen alone. Synergistic effect occurs between phosphorous and nitrogen with respect to their ability of flame retardant cotton fabric [102].

It was reported that, using triazine formaldehyde and trimethylol melamine diammonium phosphate—treated cotton, the synergistic effect was found to be dependent on the type of nitrogen present. Reeves et al. [103] suggested that, amide and amine nitrogen generally increase flame retardancy whereas nitrile nitrogen can cause reduction [104].

Weil has reviewed mechanisms of nitrogen—phosphorous interaction on cellulose. Weil pointed out in his later study that bis(methoxy methyl) iron, which lacks secondary nitrogen, ceases to be non-synergistic and, indeed, non-additive at the higher phosphorus (2%P) levels used. In addition, the presence of triazine resin with its basic tertiary nitrogen shows no increase in flame retardant activity at 1%P and antagonism at 2%P. These resins were applied with the commercial phosphonamide flame retardant, pyrovatex CP [105].

Davies and Horrocks [105] using the ratio urea formaldehyde 1:1.6 which is typical cellulosic textile formulation, illustrate that the cured resin will have a low secondary nitrogen—content and so will not show any synergistic tendency. In fact based on Weil's hypothesis, the observed antagonism of the urea—formaldehyde nitrogen should relate to its high tertiary nitrogen content. Nitrogen compounds such as amides and amines appear to catalyse the cellulose phosphate forming steps and are found to strongly synergize the action of phosphorus in cellulose systems.

Synergistic interaction between phosphorus and nitrogen was studied with various finishes, using the Limiting Oxygen Index (LOI) for evaluation. Clearly indicated the increasing of (LOI) value with the P% as the N% increased, or the increasing of (LOI) value with the N% as P% increased [99].

10.2.5 Types of Flame Resistant Finishes

Flame-retardants can be distanced into reactive and additive flame-retardants. Reactive flame-retardants are reactive components chemically built into a polymer molecule. Additive flame-retardants are incorporated into the polymer either prior to, during or (most frequently) following polymerization.

Classification of flame retardants

Flame-retardants based on different conditions were classified into four classes [59, 60, 106] these classes are (a) Nondurable flame resistant finishes, (b) Semidurable flame resistant finishes, (c) Durable flame resistant finishes and (d) Weather resistant flame retardants durability, nature of the compounds and methods of incorporation to the host polymer.

Flame-retardant chemicals based on nature of the compounds are divided into five families [65, 74, 107–110]. These are inorganic, halogenated, organo-phosphorus, halogenated phosphates and nitrogen-based flame-retardants.

10.2.5.1 Flame Retardants Based on Durability

Nondurable Flame Retardants

Nondurable flame retardants are suitable for use on cellulosic materials. The chemicals easily removed out of textiles when exposed to weather, leached, or laundered. It is should be treated again after each laundering. Even it is not laundered, it should be retreated again each 6 months because many of the nondurable type retardants crystallize on the surface of a fabric after having diffused from the inside of the fibre [54, 59, 60, 106].

The most important examples of this group are:

(a) Borax (Sodium Borate $Na_2B_4O_7\text{-}10H_2O$) and Boric Acid

Fabrics treated with this retardant are flame resistant but have afterglow which can persist from about 30 s to several minutes [54, 60].

(b) Borax (Sodium Borate $Na_2B_4O_7\text{-}10H_2O$) and Diammonium Phosphate $(NH_4)_2HPO_4$.

This flame retardant formulation applied to cotton fabrics by dissolving equal parts of borax and diammonium hydrogen phosphate in water [54, 60].

Semidurable Flame Retardants

Semidurable flame retardants can be defined as those that withstand one or more laundry cycles, with the upper limit being about 15 mild laundry cycles. The main advantage they have over the durable type, is lower cost [54, 111–115].

This class is exemplified by phosphorous compounds that are slowly dissolved and become resistant to leaching as well as to few mild launderings [112].

The most obvious means of attaining semidurable flame resistance is the application of insoluble salts. It must be taken into consideration that the flame retardant effect of the simple inorganic salts are based on their capability of decomposing in heat and releasing strong acid or alkali which is responsible for the reduction of flame propagation [113].

The most important examples of this group are:

(a) Cellulose Phosphates

A solution of urea and diammonium phosphate was padded onto fabric; the fabric was then dried for about 7 min at 175 °C. By this technique, 10–15 % esterification is achieved easily, but cellulosic fibres are severely tendered during the process. The better tensile properties are obtained through very careful curing conditions and using formulation that would fix about 3 % phosphorus in the fabric [54, 111, 114, 115].

(b) Cyanamide-Phosphoric Acid Process

A mixture of dimethylol dicyanamide and ammonium phosphate or phosphoric acid will polymerize to form an insoluble resin in cellulosic fibres, so, this modification cause less tendering of fabric. Other modifications involved replacement of urea with a mixture or diguandine thiosulphate with methylol melamine.

In a somewhat related process a pre-condensate of urea and ammonium phosphate could be insolubilized with CH_2O to produce semidurable flame resistance. Semidurable flam resistant finishes closely resembling those made from urea and H_3PO_4 could be obtained by reacting ammonia with phosphorus oxychloride [54, 62, 111].

Weather-Resistant Flame Retardants

Weather resistant and flame resistant finishes are used extensively for many materials. Water—soluble flame resistant finishes are not weather resistant because rain and humid atmospheres readily remove them. The weather resistant and flame resistant finishes may be divided into two broad groups; (a) inorganic oxides, generally have good resistance to degradation by sunlight, however, they are poor flame resistant finishes and must be used in combination with some other material, such as chlorinated paraffin and (b) organo phosphorous compounds, generally degraded by ultraviolet light and must be protected by some additional shielding materials [62, 111, 116, 117].

Durable Flame Retardants

Durable finishes are durable to multiple launderings. These are more complex and difficult to apply. Although literature mentions a large number of treatments, only a small number has survived the test of time. These include phosphorus–based compounds, pre-condensates and fibre reactive compounds, requiring multiple process steps, heat treatments ammonia treatment [62, 118].

Some of the more important requirement for ideal durable retardant is the following:

- Capability to impart fire resistance, that is, both flame and glow resistance
- Applicability to any weight fabric and preferably from water solutions
- Easy of application, preferably on existing finishing equipment without causing hazards
- Adequate ability to withstand laundering and dry cleaning
- Lack of physiological action
- Production of tough char when exposed to a fire or high-energy radiation
- Exertion of little or no adverse effect on the physical properties of the fabric
- Resistance to bleaches, particularly hypochlorite type, Reasonable cost [62].

Durable flame retardant can be applied to the surface of fibres and/or penetrate inside the fibres. To be durable on the surface the retardant materials could be probably a polymer or bonded to the surface with a polymer. Best results from surface deposits are obtained by using thermoplastic polymers.

The retardant generally impart stiffness or adversely affect some other physical property to the cellulosic fabrics because the weight add-on required imparting flame resistance by surface deposition ranges upward from about 8 %.

Using another flame retardant inside the fibre can reduce the necessary amount of thermoplastic flame retardant. Flame retardant that is applied inside cellulosic fibres can be made impervious to laundering by either of three methods:

1. Introduction of chemical substituents on the cellulose
2. Crosslinking of cellulose
3. In situ polymer formation

Use of flame retardants that crosslink cellulose molecules through primary valence bonds generally decreases tensile properties and increases resilience [112].

Through in situ polymerization technique, flame-retardants materials can be fixed in cellulosic fibres without adversely affecting strength. It is actually increases the breaking strength of fabrics without imparting a noticeable amount of stiffness or resilience [116, 117].

Therefore, one can conclude that a typical flame retardant formulation will contain:

- Reactive Phosphorous Compound

N-methylol compound (which polymerize with the phosphorous compound and helps to bind the flame retardant to the fabric.

- Catalyst and/or buffer and softener and wetting agent [119–122]

Considerable effort has been expended in recent years on developing flame retardant durable press (FR-DP) finishes for light weight fabrics. The efficiency of phosphorous flame retardant compounds has been enhanced by incorporating the N-methylol crosslinking agents through N-P synergism [112].

The most important examples of this group are:

(a) Tetrakis(Hydroxymethyl)Phosphonium Derivatives

The bulk of today's durable flame retardant for cellulose centres around the use of derivatives of tetrakis(hydroxymethyl)–phosphonium salts (THP). These derivatives can be applied by padding, drying, curing and oxidizing to yield serviceable flame-retardant fabrics. Add-ons are high and the handle of the fabric is stiffer so the finish is normally used for protective clothing applications [62, 123].

- Tetrakis(Hydroxymethyl) Phosphonium Chloride (THPC)

THPC is the most important commercial derivative and it is prepared from phosphine, formaldehyde and hydrochloric acid at room temperature. It contains 11.5 % phosphorous and it is applied by a pad-dry-cure → oxidize → scour process.

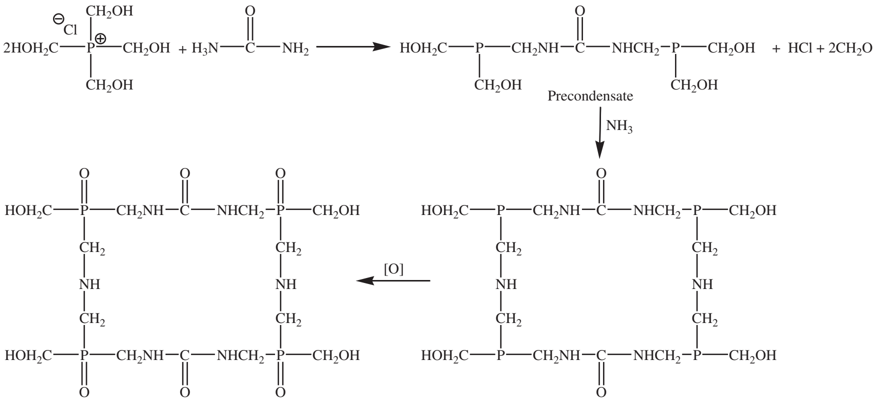
$$PH_3 + 4CH_2O + HCl \rightarrow (HOCH_2)_4P^+Cl^-$$

The compound is highly reducing in character and the methylol groups condense with amines to form insoluble polymers. It is applied with urea, dried and cured. Control of pH and the oxidation state of the phosphorus is important in determining the flame retardant properties and the durability of the finish. HC1 releasing may cause tender to fabric during curing. The final step in finishing requires oxidation of P^{+3} to P^{+5} with hydrogen peroxide. This step must be controlled to prevent excessive tendering of the fabric. An alternative to the THPC is THPS. Sulphuric acid is used instead of HC1 and the corresponding phosphine sulphate is formed in place of the phosphine chloride [62, 123].

- THPC-Urea Pre-condensate

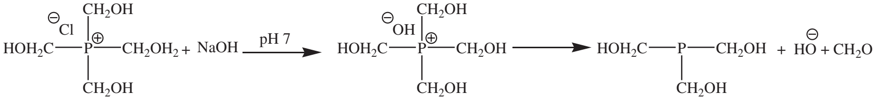
Albright and Wilson replace heat curing with an ammonia gas curing at ambient temperature. This minimizes fabric tendering associated with heat and acids. A Pre-condensate of THPC with urea (1:1 mol ratio) is applied, dried and the fabric passed through an ammonia gas reactor. An exothermic reaction creates a polymeric structure within the voids of the cotton fibre [120, 123]. The ammonia cure gives a P:N ratio of 1:2. Weight percentages of the respective elements should be

P, N >2 %. To enhance durability and light fastness of dyes, P^{+3} is oxidized to P^{+5} with hydrogen peroxide [116, 117].



- Tetrakis(hydroxymethyl)phosphonium Hydroxide (THPOH)

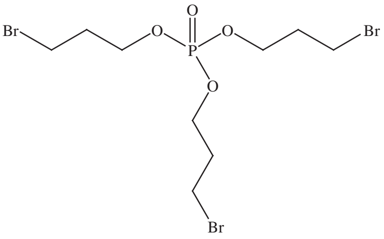
From the forgoing discussion, THPC usually partly neutralized with amines, amides and/or alkali. Complete neutralization of THPC with sodium hydroxide yields a compound referred to as THPOH. The distinction between THPC used in a partially neutralized condition and THPOH is difficult to define. If the curing agent is basic as is ammonia, the distinction become meaningless [62, 111].



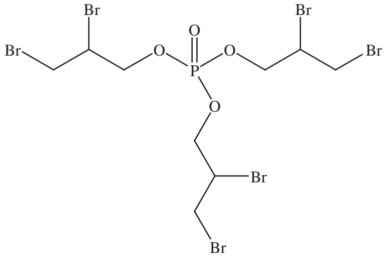
THPOH-ammonia has received a great deal of commercial attention. The major advantage over THPC is reduced fabric tendering and reduced stiffness. Fabrics padded with THPOH give off formaldehyde during drying [62].

(b) Phosphate Esters with Bromine as Durable Flame Retardants [62, 111]

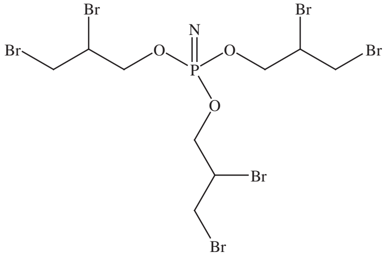
- Bromoform-triallylphosphate ester polymer



- Tris (2,3-dibromopropyl)phosphate



- Bromine-contaning phsphonitrilates.



(c) Azriridinyl Compounds [62, 111]

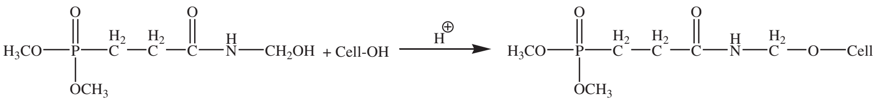
1. APO—THPC
2. APS—THPC
3. APO
4. APO—Diammonium phosphate
5. APO—Thiourea.

(d) Phosphonates and Phosphine Oxides as Flame Retardants [62, 111]

1. Phosphonomethyl cellulose.
2. Allyl phosphonate
3. Trichloro methyl phosphene and phosphene oxide.
4. N-methylol amide of phosphene and phosphene oxide.
5. Phosphopropionamides.

(e) N-Methyloldimethyl Phosphonopropioamide (PYROVATEX CP)

Pyrovatex CP provides a method of attaching phosphorus to cellulose making use of N-methylol reactivity with cellulose. It is applied with a methylolated melamine resin using a phosphoric acid catalyst by a pad-dry-cure process. The high nitrogen content of melamine provides synergistic activity to the phosphorus of the flame retardant [115, 123].



$$H_3CO-\underset{OCH_3}{\overset{O}{\overset{\|}{P}}}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2OH + \text{Cell-OH} \xrightarrow{H^{\oplus}} H_3CO-\underset{OCH_3}{\overset{O}{\overset{\|}{P}}}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\overset{H_2}{C}-O-\text{Cell}$$

Fabric stiffening occurs when sufficient chemical is applied to give 2–3 % phosphorus on weight of fabric. In addition, the acid may cause high strength loss if left in the fabric after curing; therefore, it is desirable to wash the fabric after the curing step [62] (Fig. 10.16).

The finish tends to produce smoke in the curing oven. The smoke is composed of volatile fragments of the finish, which condense in the cooler reaches of the oven. The condensate may drip back onto the fabric causing unsightly spots [62, 116, 117, 123]. Figure 10.17 explain the proposed reaction between pyrovatex and melamine formaldehyde [55, 124].

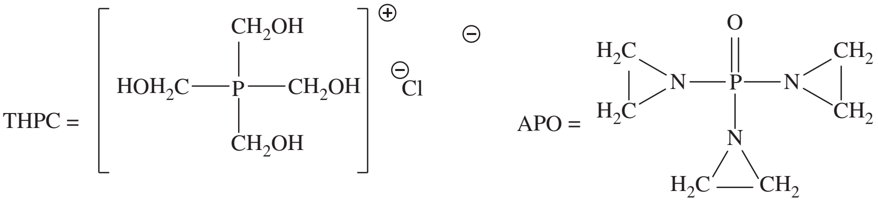


Fig. 10.16 Chemical structure of APO and THPC

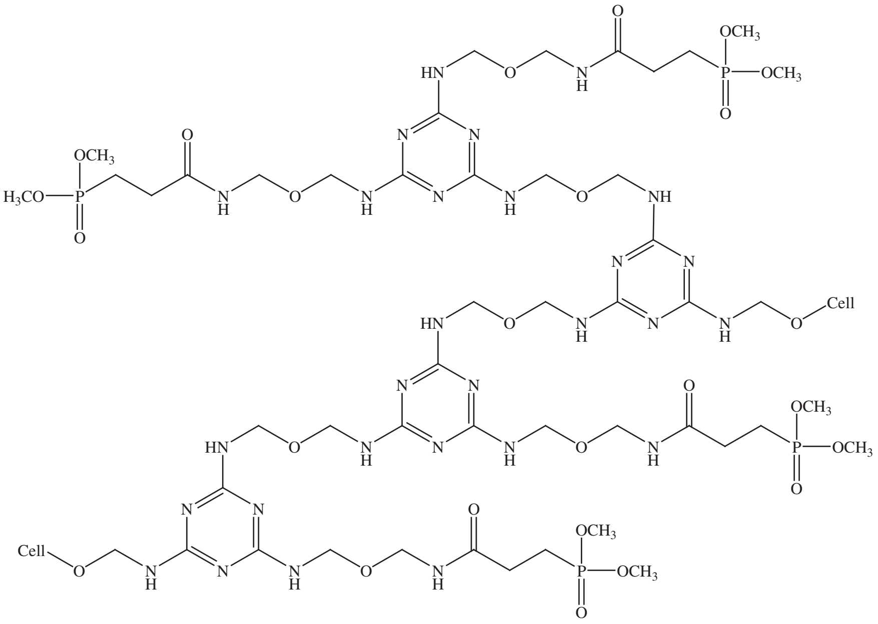


Fig. 10.17 Proposed reaction between pyrovatex and melamine formaldehyde [55, 124]

(f) Phosphono Acetamide [62, 111]

1. Inorganic durable flame retardants.
2. Antimony trioxid—chlorinated parafines
3. Antimony titanium complex.

10.2.5.2 Flame Retardants Based on Nature

Inorganic Flame Retardants

The inorganic compounds are non-combustible materials and thus physically dilute the amount of combustible polymer in the solid phase. Rothon [125] discussed several inorganic flame retardant systems. Metal oxide residues are formed during the decomposition of the inorganic systems.

By the early 1970s the main inorganic flame-retardants used were Alumina trihydrate (ATH), zinc borate and antimony compounds [73, 75]. Although antimony was one of the most popular and frequently used compounds in flame retardant systems over the years, it was expensive and thus used sparingly [75].

Aluminum hydroxide ($Al(OH)_3$), magnesium hydroxide [$Mg(OH)_2$], ammonium polyphosphate and red phosphorus are the main flame-retardants in this group, which represents about 50 % by volume of the worldwide flame retardant production. In order to achieve necessary improvements in flame retardancy, metal hydroxides are employed alone or in combination with other flame-retardants. Antimony compounds (e.g. antimony trioxide) are used as synergistic co-additives in combination with halogen compounds to enhance fire characteristics such as smoke reduction or afterglow suppression. Ionic compounds have a very long history as flame-retardants for wool or cellulose based products.

Unfortunately, in practice very high dosage levels (50–60 %) of the inorganic fillers are needed in the polymer in order to be effective. The name-retarded material should also be processed at temperatures below 220 °C [109].

Alumina trihydrate (ATH) is the least effective in terms of dosage, but also the least expensive of all flame-retardants. Aluminum hydroxide (alumina/trihydrate) ATH decomposes when exposed to temperatures over 200 °C, which limits the polymers in which it can be incorporated. Magnesium hydroxide is stable at temperature above 300 °C and can be processed into several polymers. In the recent time, scientists have been using combination of the metal hydroxides in the concept of nanotechnology to improve the flame retardancy of polymer composites. This approach involves the dispensing of inorganic filler in a nanoscale as flame-retardants into a polymer matrix [126].

Antimony Compounds

For many years now, antimony based inorganic compounds have been used for flame retardants, for example Sb_2O_3, Sb_2O_5 and Na_3SbO_4 [109]. Unfortunately, antimony based compounds are very expensive. The basic Na_3SbO_4 is ideal for polymers which hydrolyse when processed in the presence of acidic additives. Currently antimony compounds are not used as flame retardant on their own, but are used as synergists with other flame retardants. The addition of antimony compounds to halogen systems can increase their efficiency considerably and thus reduces the total additive loading in the polymer. Antimony trioxide on its own has been reported to be a catalyst for carbon oxidation [127]. However, more recent studies showed that antimony trioxide has an inhibiting effect on char oxidation [128, 129] when used with other inorganic fillers. Unfortunately, a chemical explanation for this unexpected effect wasn't given.

Antimony trioxide is one of the most widely used flame-retardants [73, 75, 109, 110]. Antimony trioxide is used as a synergist. It is utilized in plastics, rubber, textiles, paper and paints. Antimony oxides and antimonates must be converted to volatile species. This is accomplished by the reaction of halogen acids and antimony containing materials at fire temperatures to form antimony trihalide or antimony halide oxide which suppress flame propagation. Other antimony compounds include antimony pentoxide, available primarily as a stable colloid or as a re-dispersible powder. It is used in fibre and fabric. Sodium antimonate is recommended for formulations in which deep tone colours are required.

Boron Compounds

Boron compounds are also widely used as flame-retardants [109]. Compounds such as borax (sodium borate), zinc borate, barium metaborate ($BaB_2O_4.XH_2O$) and ammonium fluoroborate (NH_4BF) are well known retardant systems. Boron compounds act in both the condensed and vapour phase as fire suppressants. Most boron complexes are Lewis acids, which promote crosslinking of the polymeric material on thermal degradation and thus minimizing decomposition and volatile combustibles. Boron compounds can also react with the hydroxyl group in polymers containing such groups (e.g. cellulose) to form a glassy ester. This ester forms a char coating on the substrate surface and reduces solid-state carbon oxidation by protecting the underlying material. Moreover, it is common knowledge in commercial practice that the addition of zinc borate to metal hydroxide flame retardant systems can help to reduce the afterglow effect.

The most widely used in this class are boric acid (H_3BO_3) and sodium borate (borax; $Na_2B_4O_7.10H_2$). They are primarily used for cellulosic material such as cotton, paper, and roofing thatch [130]. They are effective in decreasing afterglow time and lengthening of ignition time; although their use is limited to products for which non-durable, flame retardancy is acceptable since both are very water-soluble.

Zinc borate is however water insoluble and is mostly used in plastics and rubber products. It is used as a complete or partial replacement for antimony oxide in PVC, nylon polyolefin, epoxy, etc. It functions as a flame retardant and smoke suppressant in condensed phase.

Silicon Compounds

There is a renewed interest in using silicon-based flame retardants as substitutes for the halogens or phosphorus [131]. Almost all forms of silicon have been explored: silicones, silica, organosilanes, silsesquioxanes, and silicates. The most common flame retardant based on silicon is in the form of polyorganosiloxane, in particular, polydimethylsiloxane (PDMS). The flammability of the block copolymers of various types of polycarbonate (PC) and poly(ether imide) with PDMS [132] show significant decreases. Silicon can also be incorporated into the branches of the polymer chains [133]. Under certain cases, the addition of silica can also affect the flammability properties of materials [134]. The formation of a silicon-based protective surface layer appears to be the flame-retardant mechanism for silicone and silica systems. Polycarbosilane, polysilastyrene, and polysilsesquioxane pre-ceramic polymers are shown in Fig. 10.18, are also used to blend with various thermoplastics, [135, 136].

Nanoparticles of ZnO and amino functionalized silica have been used in order to functional finished cotton fabrics to produce technical textile with high performance, regarding the environmental aspect [137]. Cotton cellulose had been activated via grafting copolymerization in order to facilitate the reaction between cellulose and nanoparticles. A novel flame retardant system consisted of diethyl

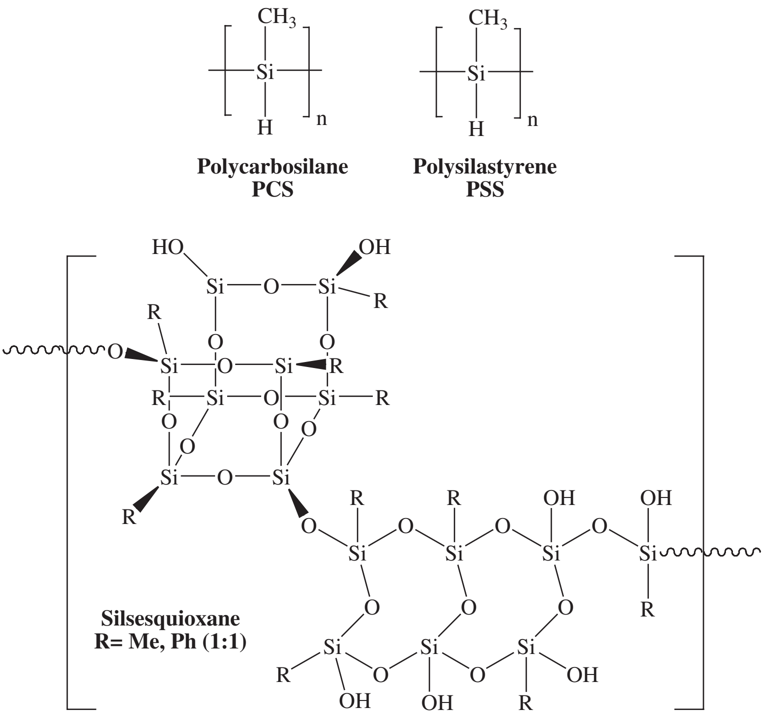


Fig. 10.18 Some pre-ceramic polymers

phosphite in combination with the ZnO and amino functionalized silica nanoparticles had been investigated. The performed treatment helps to form more nonflammable char residue and increases char formation after heating in addition to the improvement of the water repellency property. Nano ZnO was investigated as a novel flame retardant for cotton and fabrics.

In addition, the presence of phosphorus deposited on the diethyl phosphite treated samples is the most effective parameter in the char forming and decreasing the flammability of the treated fabrics [137].

Jia and Levalois-Grutzmacher [138], found that with argon plasma treatment, it is possible to polymerize a silicon-based acrylate monomer, in this case 3-(acryloy loxy)propyltrimethoxysilane (APTMS). However, APTMS is found to confer little or no flame retardant properties on cotton textiles. When introduced as a physical mixture with diethyl (acryloxyethyl) phosphoramidate (DEAEPN), the presence of Si-O bonds in APTMS does not contribute towards any synergistic effects with phosphorus and nitrogen in DEAEPN on the flame retardancy of cotton textiles.

Clays

Recently, there is a great interest in the flammability properties of polymer-clay (layered-silicate) nano-composites [139, 140].

Clays can be used as flame retardant systems. Experiments showed that the heat release rate—the most important parameter for predicting fire hazard—is reduced by 63 % in a nylon-6-clay nano-composite containing 5 % and of a modified montmorillonite clay [76]. Nano-composites used are clays. According to Oilman Kashiwagi, [76] the clay additive does not degrade the overall material properties and caused no increase in carbon monoxide or soot levels during combustion.

Phosphorus Compounds

Red phosphorus is effective as a flame retardant in polyurethane foams, polyamides and phenolic applications. Ammonium polyphosphate is mainly applied in intumescent coatings and paints. Intumescent systems are materials that puff up to produce foams [107]. Owing to these characteristics, they are used to protect materials such as wood, plastics and steel from high temperature. Other inorganic flame-retardants as ammonium sulfamate (NH_4SONH_2) and ammonium bromide (NH_4Br) are mainly for cellulose-based products and in front forest fighting.

Other Metal Compounds

The effect of the metal cation on the intumescent behaviour and char formation was studied. Metals, representative of the main groups in the periodic table are listed below:

- Alkali metals—sodium [Na]
- Alkali earth metals—magnesium [Mg] and calcium [Ca]

- Main group metals—aluminium [Al] and antimony [Sb]
- Transition metals—titanium [Ti], vanadium [V], zirconium [Zr], zinc [Zn]. iron [Fe] and copper [Cu]

Potassium is known to improve char formation in cellulose (Tang and Neill 1964) and in polyamide 6 (nylon 6) when used as synergist with silica compounds [76].

Potassium nitrate can also be used as a flame retardant in nylon 6 as it improves charring of the polyamide [141]. In addition, potassium bitartrate showed intumescence and char formation on its own [72]. It has also been found poly(sodium styrene sulphonate) is a flame retardant providing intumescent char formation [142].

Copper Cu^{+2} complexes can act to improve char performance [133]. Copper is also added to halogen flame retardants as a smoke suppressant [69]. This is most likely due to the condensed phase reactions such as charring caused by the copper.

Ebdon et al. [143] found that vanadyl acetylacetonate ($VO(CH_3COCHOCH_3)_2$) and VOCb increased the LOI of styrene/4-vinyl pyridine- and methylmethacrylate/4-vinyl pyridine copolymers by forming an intumescent char on the surface. The addition of Zn and Ni had little or no effect on char formation.

Other very popular flame-retardants are metal hydroxides such as aluminum trihydrate (ATH) and magnesium hydroxide [69, 72, 73, 144, 145]. Magnesium oxide and magnesium carbonate ($Mg_2(CO_3)_3(OH_2)$) are also used [65, 66, 72, 73, 75, 109, 146]. In some instances, calcium compounds such as calcium carbonate and calcium hydroxide, calcium sulphate and calcium oxide are also used [65, 66, 72, 75, 109].

Zinc compounds were also used. They mainly act as a source of boron (zinc borate), which helps with smoke suppression and to stabilise carbon chars [65, 66, 69, 72, 73, 75, 109, 147] or as a source of phosphate ($ZnPO_4$)—the catalyst for intumescence [148].

To isolate the specific effects of the metals on intumescence, carbon char yield and thermal degradation, a common organic compound (backbone) had to be used. Acetylacetone, i.e. 2,4-pentanedione was selected for this purpose. It forms very stable complexes with most of the metals. The chemical properties of acetylactone are determined by the keto-enol tautomerism shown in Fig. 10.19. At moderate temperatures, it is generally accepted that the enol form predominates in the gas and liquid phases.

Acetylacetone is renowned for forming stable metal acetylacetonate complexes [149]. The metal reacts with the acetylacetonate in the enol form-to-form bonds between the two oxygen atoms and the metal ion. The inner complexes formed between the metal ions and the β-diketones are unusual since they possess properties usually associated with pure compounds, and not organometallic complexes.

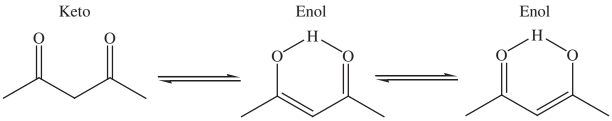


Fig. 10.19 2,4-Pentanedione (acetylacetone) and its stable isomers

Gluconic acid is a good chelating agent for most metals. Metal complexes of gluconic acid were used, e.g. sodium gluconate showed appreciable intumescence, high carbon char yield and good char properties. Calcium gluconate monohydrate, magnesium gluconate hydrate, iron (II) gluconate hydrate and copper (II) gluconate were used as commercial products. Ammonium was also used as a cation with this acid in order to be clear on the influence of the metals on intumescence and char properties.

Molybdenum compounds are also used as flame-retardants [109], and it was one of the first elements to be used as flame retardant additives for cellulose. Molybdic oxide, molybdenum trioxide, zinc molybdate and ammonia octamolybdate are used. Molybdenum trioxide acts as a condensed phase retardant by increasing char yields. Molybdenum compounds have been used as flame-retardants for cellulosic materials and in other polymers as smoke suppressants. Titanium and Zirconium compounds are used for textiles, especially wool [107].

Halogenated Organic Flame Retardants

The halogenated flame retardants are divided into three classes, namely aromatic, aliphatic and cycloaliphatic. Among the halogens, the compounds bromine and chlorine are significant as flame retardants. Fluorine compounds though expensive are ineffective because the C-F bond is too strong. Iodine compounds though effective are expensive and too unstable to be useful [74].

The thermal stability of halogenated flame retardants vary in the order of; aromatic brominated flame retardants greater than the aliphatic chlorinated flame retardant which in turn are more stable than aliphatic brominated flame retardants.

The aromatic bromated flame retardants can be used in thermoplastics at fairly high temperatures without stabilizers but at very high temperatures, they must be used with stabilizers like tin compounds [74].

Brominated Flame Retardants

Bromine-based flame-retardants are highly brominated organic compounds with a relative molecular mass ranging from 200 to that of large molecule polymers. They usually contain 50–85 % (by weight) of bromine [150]. Tetrabromo bisphenol A (TBBPA) and decabromo diphenyl ether (DeBDE) are the two brominated flame-retardants that have the highest usage by volume today.

TBBPA is an example of a flame retardant that can be used as an additive as well as a reactive. It is used in the production of flame retarded epoxy resins used in printed circuit boards. DeBDE is used in high impact polystyrene, which is in the production of television cabinets.

Other uses of DeBDE are in ABS, engineering thermoplastics, polyolefins, thermosets PVC and elastomers and textiles. Hexabromocyclo dodecane (HBCD) is a major cycloaliphatic flame retardant and its primary used is in polystyrene foam and textiles.

Chlorinated Flame Retardants

Chlorine-containing flame-retardants are divided into three classes: aliphatic, cycloaliphatic and aromatics. Chlorinated parafins are the most widely used aliphatic chlorine containing flame-retardants. The have applications in plastics, fabrics, paints, and coatings. Bis (hexachlorocyclo-pentadieno) cyclooctane is a flame-retardant having good thermal stability for chlorinated cycloaliphatic, with thermal stability comparable with brominated aromatics. It is used in several polymers especially polyamides and polyolyfins for wire and cable applications [74].

Organophosphorus Flame Retardants

The predominant phosphorus flame retardants in use in plastics and textiles are phosphorus, phosphorus-nitrogen, phosphorus-halogen and phosphate esters with or without halogen. Phosphorus-containing flame retardants are the most important material that impart durable flame resistance to cellulose [110, 151]. The major groups of additive, among organo-phosphorus compounds are phosphate esters, polyols, phosphonium derivatives and phosphonates.

The phosphate esters include trialkyl derivatives such as triethyl or triocytyl phosphate, triaryl derivatives such as triphenyl phosphate and aryl-alkyl derivatives such as 2-ethyl hexyl-diphenyl phosphate. Phosphonium salts are used to improve the flame retardancy for cellulosic products. The esters formed by reaction of the three functional groups of phosphoric acid with alcohols or phenols are excellent plasticizers. Plasticizers are mixed into polymers to increase flexibility and workability [152, 153]. Aryl phosphatem plasticizers are used in PVC based products, used as lubricants for industrial air compressors and gas turbines.

Other uses of aryl phopsphates are as pigments, dispersants and peroxide carriers, and additives in adhesives and wood preservatives.

Halogenated Phosphates

These are flame retardants that contain phosphorus and bromine or chlorine. They normally combine the flame retardancy properties of phosphorus and those of the halogens (bromine and chlorine).

Among this group, is tris (1-chloro-2-propyl) phosphate (TCPP) used in polyurethane foam. The other is the tris (2-chloroethyl) phosphate used in the manufacture of polyester resins, polyacrylates, polyurethanes and cellulose derivatives. In the bromine—phosphorus group, the commonest is tris (2,3-dibromopropyl) phosphate which has been withdrawn from use in many countries due to carcinogenic properties in animals [108].

Nitrogen—Based Flame Retardants

Nitrogen-based flame retardants are used primarily in nitrogen containing polymers such as polyurethanes and polyamides. They are also utilized in PVC and polyolefins and in the formulation of intumescent paint systems [154].

Melamine, melamine cyanurate, other melamine salts are currently the most used group of nitrogen—containing flame retardants. Melamine, melamine cyanurate are used for polypropylene, polyethylene, polyamindes epoxy and polyurethane.

10.2.6 Flammability Tests for Textile

To fully evaluate the fire behaviour of different polymers, it is necessary to develop standard tests for assessing the flammability and other combustion-related properties of polymers. Most countries have standards and codes for the classification of materials with respect to their combustion behaviour, but the experimental setup used in existing standard tests varies considerably, according to the nature, shape, and size of the polymeric materials to be tested [136]. The fire tests most commonly used are the ASTM E 84 Steiner Tunnel [155], and the ASTM E 622 National Bureau of Standards (NBS) smoke chamber [156]. However, these tests can be used only as guides and suffer from problems with precision and reproducibility.

The majority of fire tests used now are concerned with the determination of the following fire properties of materials [136, 157].

- Ease of ignition—how readily a material ignites
- Flame spread—how rapidly fire spreads across a surface
- Fire endurance—how rapidly fire penetrates a wall or barrier
- Rate of heat release—how much heat is released and how quickly
- Ease of extinction—how rapidly or how easily the flame chemistry leads to extinction
- Smoke evolution—amount, evolution rate, and composition of smoke released during stages of a fire
- Toxic gas evolution—amount, evolution rate, and composition of gases released during stages of a fire.

Among them, the oxygen concentration test is a very important ignition test, from which the limiting oxygen index (LOI) [158] can be obtained. The LOI is defined as the minimum oxygen concentration at ambient temperature needed in an inert gaseous medium for the material to achieve sustained burning after ignition. The precision and reproducibility of the results are two reasons for the wide acceptance of this method.

10.2.6.1 Vertical Spread Method of Flame Test: AATCC 1934–1969 [54, 60, 111, 159]

The vertical flame test is the most severe test. The criteria evolutions are char length, after flame removal and after vanishing of glow. Fabric specimen dimensions are 1.5 × 72 in., conditioned at 70 °F and 65 % relative humidity. The specimen mounted in a holder kept in a cabinet, is subjected to standard flame (gas burner) at its lower edge, under controlled condition. The fabric specimen is suspended in a vertical position and flame is applied along the fabric width. The rate of flame spread is recorded and the flaming time, after glow time and char lengths are measured.

10.2.6.2 Horizontal Spread of Flame Test Method 5906–CCC–T–1916 [60, 160]

Several tests have been designed for measuring the spread of flame on horizontally placed fabric specimens. In federal specification method 5,906 specimen strips of 12.5 × 4.5 in. oven-dry fabric are used. Ignition is affected in one end of the sample, and the rate of burning is measured. In method 5,900 the ignition is effected in the centre of the horizontal specimen and the largest dimension of the charred area is reported. A Germen method similar to 5,906 was also announced. Specimens of 35.5 × 10 cm, is clamped of two matching rectangular frames and held horizontally in a certain conditioned at 20 °C and 65 % humidity, is ignited for 18 s by a propane gas burner of specified dimensions applied to the edge of the specimen the time required for the lower of the flame front to travel across the specified length is measured.

10.2.6.3 The 45° Angle Test: AATCC 1933–1962 [60, 161]

The test is designed to indicate the textiles, mainly used for apparel and applicable for easily flammable fabrics, which ignite easily and, once ignited, burned with sufficient intensity and rapidity to hazardous when worn. The test was first developed by AATCC following the adoption of flammable fabrics act in 1954. Oven-dry specimens of 2 × 6 in. are used in the test. The specimen is held at 45° in a rack placed in ventilated chamber containing an automatic timing device and a standardized ignition medium. The flame applied is of 5/8 in. length. The distance of fuel nozzle from the fabric surface is 5/16 in. The distance from the central point of flame impingement on the face of specimen to stop-cord made of mercerized cotton sewing thread 5 in. The time of ignition is adjusted 1 ± 0.05 s. The time of flame spread, including ignition from the impingement point to the stop-cord (5 in.) is measured. Flaming times higher than 3.5 s for textile without a raised fibre surface or 7 s for textiles with raised fibre surfaces are considered of “normal flammability”. Textile of intermediate flammability with raised fibre surfaces have a time of flame spread between 4 and 7 s. Lower times of flame spread characterize dangerously flammable textiles. The 45° test has recently been accepted in a modified form in Japan.

10.2.6.4 Ease of Ignition [111]

Oven-dry specimens of 7 × 7 in. are used. The specimen is placed horizontally and a micro burner is applied to one edge. The time needed to ignite the specimen is measured.

10.2.6.5 The Limiting Oxygen Index (LOI) Test ASTM 2863 [60, 106, 158]

This test, suggested in 1966 for testing the flammability of polymers. It has been recently adapted to the testing of fabrics. The (LOI) is defined as minimal volume fraction of oxygen in a rising gaseous atmosphere that will sustain candle like burning of the sample of solid polymer or fabric. A gas metring system and a Pyrex glass chimney (as a flame holder) is 15 in. high and 3.5 in. diameter.

The samples tested are in the form of 2.5 × 6 in. strips placed into a hinged U-shaped holder, while the free end of holder is held with clamps. The holder is mounted vertically in the chimney on the chimney axis. A series of known mixtures of O_2 and N_2 in varying ratios are passed upward through the chimney at a velocity of 3–11 cm/s for 1–2 min each the sample is ignited with a laboratory gas burner at its top end during the flow of mixture, the oxygen concentration below which the flame will not spread downward the entire length of samples found, and its volume fraction in the gas mixture is designated as LOI. Figure 10.20 illustrate the scheme of LOI tester.

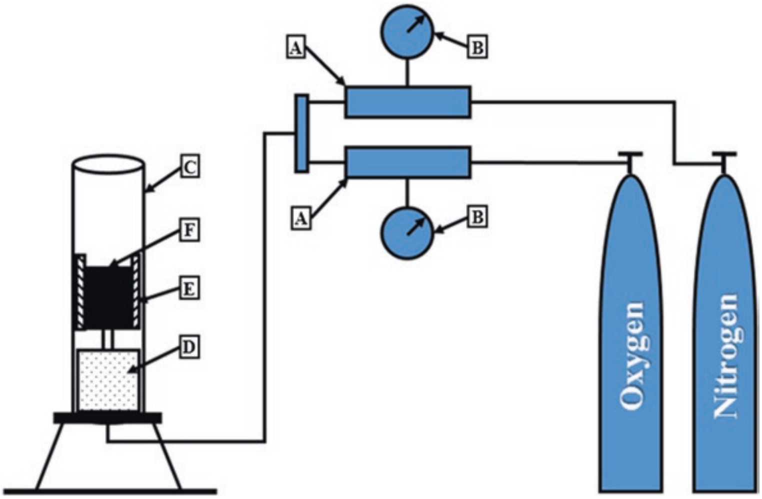


Fig. 10.20 Scheme of the limiting oxygen index (LOI) tester. *A* metering, *B* test gas, *C* pyrex cylinder, *D* glass beads, *E* sample holder, *F* test fabric

10.2.6.6 The Metal Cylinder (Carpet Flammability Test) [60, 111]

Which consists of placing a steal cylinder heated to 800 °C on a carpet for 12 s and measuring the time of flaming and the charred area.

10.2.6.7 Cigarette Test [162]

This test for household furnish like mattresses. Smouldering cigarettes (non–filter from natural tobacco) are applied at four types of locations smooth surface, tape edge, quilted location under two sheets on the mattress. Combustion distance and time for flaming and smouldering as well as char length are measured.

10.2.6.8 Pill Test DDD–C–95 [60, 163]

This test for carpets and rugs, a methylamine tablet is placed in the centre of a 6 × 6 in. carpet specimen and light with match. The tablet burns for about 2 min and the diameter of the char area is measured.

10.2.6.9 Smoke Test [156, 164]

A test specimen (7.6 × 7.6 cm) is vertically mounted and max. 2.5 cm is exposed to radiant heat and/or a gas flame in chamber (91.4 × 61 × 91.4 cm). A photometric system is used to measure smoke density.

10.2.6.10 Colorimeter Test (NBS Cone Colorimeter) Consider by ASTM E 84 and E 119 [155, 165]

The Cone Calorimeter test is probably the most widely used test method in use today to calculate the rate of heat released by a burning material. Ignitability polymer formulations can also be tested in the calorimeter. It is the bench-scale test method used most commonly for the majority of polymer fire testing and was developed in 1982 by Babraukas at the National Institute of Standards and Technology (NIST). A 100 mm by 100 mm sample (up to 50 mm thick) is placed horizontally in the apparatus and exposed to a radiant heat flux of 10–100 kW/m^2 with a spark ignition system. The effluent is monitored and temperature, gas flow rate and oxygen concentration measured. The amount of smoke produced along with carbon dioxide and carbon monoxide concentrations can be determined with some instruments. Flame retarded coatings can also be evaluated with the cone calorimeter,

Flame retarded coatings are commonly tested under fire tests developed for materials used in the construction of buildings. Examples of such tests are the

American Society for Testing and Materials (ASTM E 84 [155] and E 119 tests [165]). The Steiner Tunnel is the basis for the ASTM E 84 test. It is possibly the oldest fire test for flame retarded materials in use in North America and is used to test the surface burning characteristics of building materials. The test was developed by Albert J. Steiner of Underwriters Laboratory Inc. and Simon Ingberg and was first described in 1943. A 0.514 m wide and 7.32 m long sample is placed in the ceiling of a 7.62 m (25 ft) long tunnel with a 88 kW burner at the one side of the tunnel and an air draft forced through the tunnel at a velocity of 1.22 m/s. The flame spread is recorded as a function of time. The tunnel is also fitted with a photometer to determine smoke. The test results for some plastics are however questionable. Due to its size, large samples were needed for testing. From the 25 ft Steiner tunnel test several smaller tunnel tests were developed e.g. the 18, 8 and 2 ft tunnel tests [166].

10.3 Fire and Flame Retardancy Finishing of Cellulosic Materials and Its Composite

10.3.1 Fibres and Fabrics

10.3.1.1 Cellulose (Cotton and Rayon) [167]

There are important historical and economic reasons for the fact that, the science and technology of flame-retardants for cellulose fibres are more advanced than for other fibres and polymers. Until perhaps 25 years ago, an overwhelming proportion of all textiles used was made of cellulosic fibres.

Thermal degradation of cellulose, which added flame-retardants, has led to a partial elucidation of the mechanism of fire-retardant action by Lewis acids. The principal role of acid or acid-forming flame-retardants in cellulose is to enhance dehydration and char formation in the condensed phase, suppressing the formation of combustible volatiles in the thermal degradation process.

Phosphorus acids are particularly efficient in catalysing cellulose dehydration, and phosphorus-containing flame-retardants have been studied most extensively. In the case of natural cellulosic fibres, modification with flame-retardant compounds has been accomplished almost exclusively by finishing of fabrics. In the case of regenerated cellulose fibres, the most important approach to modification has been the incorporation of flame-retardant additives in the spinning fluid.

Flame-retardant finishes for cotton fabrics have been studied and reviewed before in a large number of other publications [4, 31, 54, 60, 100, 124, 137, 168–173]. Milestones of the evolution from simple processes involving deposition of inorganic salts (readily removed by water) to sophisticated modifications of the cellulose molecule and/or in situ polymerization of appropriate monomers are summarized in Table 10.3.

Table 10.3 Some historical compounds of flame retardants for cellulosic fabrics

Compounds	Applications
Mixtures of ammonium phosphate, ammonium chloride and borax	Linen and jute fabrics
Sodium stannate followed by ammonium sulfate to precipitate stannic oxide in situ	Cotton flannel
Chlorinated paraffin and antimony oxide	Canvas for military tentage “FWWMR” finish
Phosphorylation of cotton (ureaphosphate)	Cotton fabrics for apparel
Titanium oxychloride and antimony oxychloride	Cotton fabrics “ERIFON” finish
Trisaziridinyl phosphine oxide (APO) and Tetrakis hydroxymethyl phosphonium chloride (THPC) developed at USDA as components of durable finishing systems	All types of cotton fabrics
N-methyloldimethy1phosphonopropionamide (Pyrovatex CP)	All types of cotton fabrics
N,N′,N″ Trimethylphosphoramide with trimethylol melamine (MCC 100/200/300)	All types of cotton fabrics
Vinyl phosphonate oligomer (Fyrol 76) copolymerized with N-methylol acrylamide	All types of cotton fabrics
Methyl phosphonicdiamide, chloromethylphosphonic diamide	All types of cotton fabrics

Flame-retardant finishes based on chlorinated paraffins and antimony oxide in conjunction with resin binders were developed for tent fabrics. Large amounts of finish (up to 60 % solids applied based on fabric weight) were used, impairing the flexibility and air permeability of the treated fabrics. However, the finish succeeded in combining flame resistance, water and mildew resistance for a critically important application.

Attempts to obtain durable flame resistance in cotton by chemical modification of the cellulose molecule were made in the late 1940s. Work on phosphorylation of cellulose in the presence of large amounts of urea or other basic compounds to prevent acid degradation and depolymerization of the polymer [167] led to a process, which was used, on a commercial scale for a time. However, the phosphate ester linkage introduced into the cellulose is not sufficiently stable to hydrolysis to withstand repeated laundering and the presence of ion exchange sites in the modified cotton leads to replacement of NH: by metal cations with loss of flame resistance.

Reaction of cotton with titanium oxychloride and antimony oxychloride [167] enjoyed a brief period of intense interest. The development of “modern,” truly wash-resistant, or durable flame-retardant finishes for cotton fabrics began on the reactions of two organophosphorus molecules, APO and THPC (Fig. 10.16) with cellulose, with coreactants, and with each other.

Finishes based on THPC chemistry have been produced commercially for a decade, and remain important. Finishes based on APO chemistry have been abandoned primarily because of toxicity and/or suspected carcinogenic properties of the reagent (APO) and its precursor (ethylene imine).

10.3.1.2 Other Cellulosic Fabrics

In principle, approaches used for finishing of cotton fabrics are applicable to other cellulosics (rayon, linen, jute, etc.). In fact, the amounts of flame-retardant finish needed to attain a specified level of flame resistance. Commercial production of flame-resistant 100 % cellulosic fabrics by finishing has been limited to cotton, and some specific rayon fabrics [167].

Regenerated Cellulose (Rayon) Fibres

Flame-resistant rayon fibre can be used to manufacture fabrics, which are self-extinguishing in a vertical test. It has been made commercially by incorporating an alkoxyphosphazene in the spinning fluid (Fig. 10.21). The commercial fibre employs the n-propoxy compound ($R = n\text{-}C_3H_7\text{-}$) as the additive.

Other approaches in which the rayon fibre is modified by graft copolymerization reaction with a flame-retardant monomer prior to yarn manufacture have been suggested, but have not reached commercial status to date [167].

These fibres usually have flame retardant additives incorporated into the spinning dopes during their manufacture, which therefore yield durability and reduced levels of environmental hazard with respect to the removal of the need for a chemical flame retardant finishing process (see Table 4.8). Additives like phosphorus-based and so are similar to the majority of these fibre finishes in terms of their mechanisms of activity (condensed phase), performance and cost-effectiveness [89].

This fibre not only has removed the need for phosphorus, but also chars to form a carbonaceous and silica-containing mixed residue, which offers continued fire barrier properties above the usual 500 °C where carbon chars will quickly oxidise in air [89].

Cellulose Acetate and Triacetate

Cellulose acetate and triacetate fibres, or cellulose ester fibres which made by acetylation of natural cellulose are thermoplastic. They melt at relatively low

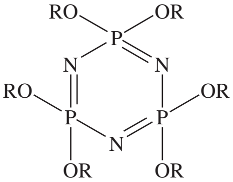


Fig. 10.21 Chemical structure of alkoxyphosphazene

temperature [174], they ignite, and they can propagate the flame even though they drip while they continue to burn. The only method used to attain fire resistance in cellulose acetate and triacetate fibres is the incorporation of a flame-retardant additive (specifically, 2,3-trisdibromopropyl phosphate) into the spinning solution before extrusion. The bromine-containing product (flame-resistant acetate) obtained is somewhat more resistant to ignition than the unmodified acetate. If a non-thermoplastic component is present in the system, it acts as a wick for the molten acetate or triacetate polymer and burning is sustained. In this case, the amount of flame-retardant additive commonly used in spinning (about 10 % based on polymer weight) is not sufficient to impart flame resistance and self-extinguishing behaviour [167].

10.3.2 Flame Retardant Cellulosic Blends

Blends are textile materials made from yarns containing two or more different fibres whether synthetic or natural. Blend fabrics have attained great commercial importance and have afforded opportunities for optimal utilization of fibre properties in textile products.

In practice, a number of technical limitations including dictates limitations: [175]

1. Compatibility of fibres during spinning or fabric formation; fibres must be available with similar dimensions and be processible simultaneously with other types on the same equipment.
2. Compatibility of fibre and textile properties during chemical finishing; for instance, flame retardant cotton treatments must not adversely influence the characteristics of the other fibres present in the blend during their chemical application.
3. Additivity and, preferably synergy, should exist in the flame retardant blend; it is well known that with some flame retardant blends, antagonism can occur and the properties of the blend may be significantly worse than either of the components alone [175].

Flammability and flame resistance of blends have received attention since 1968, and it was soon established that modification of these multicomponent substrates with flame-retardants poses special problems [167, 176]. The large number of variables in the substrate (specific fibres, fibre content or percentage, melting vs. non-melting behavior, etc.) further increases the complexity of these problems.

The most important blend fabrics are those made from polyester and cotton, generally (but not necessarily) containing 50 or 65 % polyester. Modification of these fabrics with flame-retardants can be approached by (1) blending modified (flame-resistant) polyester fibre with cotton; (2) finishing the polyester/cotton blend fabric with flame-retardants; (3) a combination of (1) and (2) [167].

All these approaches have been explored, generally utilizing flame-retardant compounds, which showed effectiveness on polyester and on cotton. The use of modified polyester does not provide an adequate level of flame resistance since melt drip is inhibited by the presence of cotton.

Modifications of the polyester specifically designed for approach (1) have not been reported, and research and development efforts have been directed primarily towards approaches (2) and (3)-namely, finishing.

10.3.3 Flammability of Natural Fibre Composites

As with composites reinforced with glass or other synthetic fibres, natural fibre reinforced composites (NFRC) comprise a polymer matrix that is reinforced with natural fibres. A wide range of fibres, mainly plant, and polymer matrices utilized have been reported in Table 10.4 [31, 177, 178].

The flammability properties of the composite are different from the component materials and factors such as the structure of the composite, adhesion between the fibres and the matrix, the type of matrix polymer, and the type of fibre all play roles in determining these properties [31, 179].

Natural fibres are non-thermoplastic and their decomposition (pyrolysis) temperature is less than their glass transition and/or melting temperatures [21, 23]. Unlike protein fibres, plant fibres has poor fire resistance; for example, cotton has a LOI value of 18–20, whereas wool has a LOI value of 25 [180].

Table 10.4 Examples of thermoplastic and thermoset matrix–natural fibre composites

Fibre	Polymer matrix								
	Thermoplastic					Thermoset			
	PP	PE	PA66	PS	PVC	Epoxy	PET	Vinyl ester	Phenolic
Cellulose[a]	√	√	√	√	√	√			
Flax	√	√				√			
Jute	√	√				√	√	√	√
Sisal	√	√		√		√	√		
Kenaf	√					√			√
Ramie	√								
Hemp						√	√	√	√
Bagasse	√								√
Bamboo	√					√	√		
Pineapple		√					√		
Wood flour/fibre	√	√		√	√		√		

Adapted from Puglia et al. [177], and Blicblau et al. [178]

[a] Includes cotton

The thermal degradation of plant fibres involves a number of processes including the desorption of adsorbed water, cross-linking of cellulose chains with the evolution of water to form dehydrocellulose, decomposition of the dehydrocellulose to yield char and volatiles, formation of levoglucosan, and decomposition of the levoglucosan to yield flammable and nonflammable volatiles and gases, tar, and char [23, 32, 181].

Manfredi et al. [30] found that, the thermal degradation of sisal and jute was similar, with the main peak at 340 °C, whereas the flax started to degrade at higher temperatures, with the main peak at 345 °C. Slight variations in the flammability of different plant fibres can be attributed in part to the chemical composition of the fibres.

10.3.4 Wood and Paper

The importance of wood and wood-based products (insulation board, hardboard, and particle board) in our environment is obvious. Similarly, enormous quantities of paper and paper like products are consumed daily, frequently in situations where fire safety considerations are important [167].

Wood and paper products consist essentially of cellulose. Thus, flame-retardant compounds that inhibit flammability of cellulose are, in principle, effective for wood, paper, and cellulosic textiles. It is clear, however, that flammability and performance requirements, durability of flame resistance, critical side effects, and economics are different for these products.

When wood is progressively heated at raised temperatures, changes begin to occur in its structure, accelerated by further increase in temperature [182]. The three polymeric components in the wood begin to thermally decompose to a mixture of volatile gases, tar (levoglucosan) and carbonaceous char. The decomposition is often regarded as the superposition of the individual constituent's decomposition mechanisms: hemicellulose decomposes first [180–350 °C] followed by cellulose [275–350 °C], and lignin [250–500 °C] [182, 183]. The thermal stability of lignin is considered to be due to its heavily cross-linked structure and high molecular weight [182, 184].

The subject of flame-retardants for cellulose must be divided into its logical components; namely, wood and wood-based products, paper and paper-based products.

10.3.4.1 Wood and Wood Based Products

Modification of wood and wood-based products with flame-retardants aims at preventing ignition and at reducing the rate of flame spread if ignition occurs.

Fire retardants are typically either coated onto the surface of the wood, or impregnated into the wood structure using a vacuum-pressure technique, although other technologies, such as plasma treatments [185], are being investigated.

The structure of wood being as similar to that of a sponge, with cell cavities and cell walls when impregnating.

To protect the structure from fire, these walls must coat with fire retardant. First, the vacuum removes the air from the cavities to create space for the fire retardant solution, which is then forced deep into the wood under high pressure.

Painted, sprayed or dipped into a solution of fire retardant are the ways to apply a protective surface coating to wood. Superficial treatments, such as paints, are often thought to be attractive for the ease with which they can be applied, and for the comparatively small amount of material required for fire protection. However, the associated re-application requirements and surface damage possibilities are considerable problems for the end-user.

Fire retardants exert their influence on the combustion of wood by numerous approaches. All the treatments are aim to delay the time to ignition of wood, reduce the rate of heat release during combustion [186] and reduce the surface spread of flames. The modes of action (how they work) are described briefly.

Browne [187] provided an in-depth literature survey on these concepts and summarised them into four basic theories. These are chemical, coating, thermal and gas theories; however, these strategies are by no means mutually exclusive because two or more of them may be, and probably are, operative in a given case.

Chemical mechanisms are exhibited by most commercial fire retardants for wood where the pyrolysis of wood is directed towards the production of increased char and water, and fewer volatiles. Coating theories suggest that the fire retardant coats the wood fibres to provide a ‘blanket’ of protection, and prevent the escape of flammable vapours and access of oxygen. Fire retardants displaying thermal action can operate in one of three ways: provide thermal insulation to the wood, absorb the surrounding heat by endothermal reactions, or increase the thermal conductivity of wood in order to dissipate the heat from the wood surface. Gas theories suggest that gases released by the fire retardant either dilute the flammable gases produced by wood to prevent the formation of a flammable mixture, or inhibit chemical reactions in the flame so that combustion is incomplete and less heat is available to sustain burning. Examples of substances used for each of the mechanisms described are outlined in Fig. 10.22 [182].

It can be approached either by impregnation of the substrate with flame-retardants, or by surface coatings. The former method has a long history, dating back to the first century B.c., when alum and vinegar solutions were used as fire-retardant treatments for wood. Although the flame-retardant chemicals are relatively inexpensive, the processing cost is high and the treatment increases the cost of the wood or wood products by 50–100 %.

The chemicals and treatment processes used commercially have been developed primarily from empirical knowledge and pragmatic observations over the years. Recent research on the manner in which flame-retardant compounds alter pyrolysis and combustion processes in wood cellulose now provides a conceptual framework for established approaches and for new developments as well [182].

It is now generally accepted that flame-retardant chemicals that are effective for cellulose (specifically wood) alter the course of thermal degradation reactions in

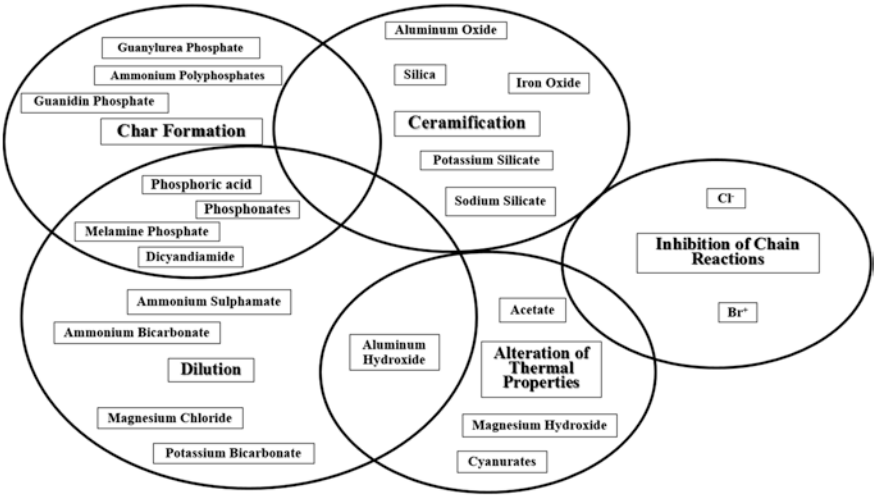


Fig. 10.22 Examples of fire retardants acting by different mechanisms [182]

Table 10.5 Thermal data for α-cellulose

Additive	Activation energy of pyrolysis Kcal/mole	Heat of pyrolysis cal/g	Max rate of heat generation cal/g/min
None	33–35	88	870
2 % $Na_2B_4O_7.10H_2O$	30–32	58	730
2 % $AlCl_3.6H_2O$	33–33.5	57	665
2 % $KHCO_3$	19–21	72	588
2 % $NH_4H_2PO_4$	17–19	78	635
8 % $NH_4H_2PO_4$	–	64	490

the solid phase, increasing the amount of char, water, and carbon dioxide formed at the expense of combustible degradation products (organic volatiles-tars and gases).

Volatile degradation products from treated wood provide less energy on combustion than the same weight of volatiles from untreated wood, while the char yield is significantly increased. Thermal data showing the effect of additives in α-cellulose are shown in Table 10.5 [182], and are indicative of the approaches used for imparting flame resistance to wood, involving primarily inorganic salts.

These inorganic salts are generally used in mixtures containing several compounds (e.g., 10 parts diammonium phosphate +60 parts ammonium sulfate +10 parts borax +20 parts boric acid = "Minalith formulation"). Aqueous solutions containing 12–15 % concentrations of the flame-retardant salts are used for pressure impregnation of lumber or plywood, aiming for a dry-salt retention of 2.5–3 lb/ft^3 for plywood or 2 in. lumber (and decreasing amounts for thicker lumber).

Pulp also treated before sheet formation, or the wet pressed mat may be treated before drying. Hardboards have also been treated by pressure impregnation after hot pressing. Related processes have been disclosed for particle board [54, 60].

Approaches for chemical modification of wood with organic and/or reactive flame-retardant compounds [182] are include four terms: (1) impregnation from emulsions of organic phosphates in combination with oil-borne preservatives, (2) impregnation from solvent solution of organic compounds of phosphorus and halogen, (3) impregnation with (unsaturated) organophosphorus monomers polymerized in situ by radiation and (4) bromination of lignin to produce bromolignin as the effective flame retardant.

Wood and wood-based products properly treated with fire-retardant formulations have decreased rates of surface flame spread (ASTM Test for surface burning characteristics of building materials E-84-13A [155]) and are self-extinguishing (flaming and glowing) when the external source of heat is removed.

In modifying wood by chemical treatment, the influence on many properties must be considered, including the effect of added flame-retardants on strength, durability, hygroscopicity, corrosiveness, painting, gluing, and machining characteristics. Reduced performance in some of these characteristics (in addition to the cost of fire-retardant treatment) has limited the use of wood-based products treated with fire retardants.

Many of the chemicals used as fire retardants are water-soluble inorganic salts, easily leached from the wood: therefore, the treatments are primarily limited to interior uses. Furthermore, some chemicals used in fire-retardant formulations are hygroscopic, and as water is absorbed, droplets may come to the surface and drop from the treated substrate, with consequent loss of fire retardant. Many of the inorganic salts used as fire retardants are corrosive to certain metals and alloys. Formulations can be balanced and neutralized, and commercial corrosion inhibitors added so that this does not pose a problem. However, if treated wood is exposed for long periods at high relative humidity, moisture and chemicals may be exuded on the metals, and produce various forms of electrolytic corrosion, which the inhibitors may not be able to control.

10.3.4.2 Fire Retardant of Wood-Plastic Composites

It has been noted that addition of lignocellulosic fibres to polypropylene reduces the heat release rate peak essentially. Characteristics such as heat released in combustion and mass loss rate are also reduced. However, criteria such as time to ignition and production of smoke deteriorate in comparison with pure polypropylene [188, 189]. The flammability of WPCs depends on several factors: type of raw material, structure, density, thermal conductivity, humidity, and the nature of composite [31, 190].

Fire retardants can be introduced into composites by two methods [58]:

1. Mass treatment: The addition of fire retardants to the mass during the production process
2. Surface protection: The addition of fire retardants onto the surface of the composite in the final stage of production [21, 191].

The flame retardancy of WPCs can be enhanced by several methods: [21, 58, 186]

1. Insertion of lignocellulosic natural fibres together with flame retardants before the production process by impregnation in an autoclave
2. Addition of fire retardants in liquid or solid form during the production of the composites
3. Use of non-flammable polymers and resins
4. Additior1 of nanoparticles to the composites
5. Insulation of the composites to prevent penetration of heat flux (intumescent coatings and fire barriers).

The above methods can be used together or separately. The current ecological situation dictates the new tendency of use halogen-free fire retardants.

Commonly used fire retardant compounds for wood-plastic composites are magnesium hydroxide, boric acid, ammonium phosphates and borates, ammonium sulphate and chloride, zinc chloride and borate, phosphoric acid, dicyanodiamide, sodium borate and antimony oxide. These additives are generally introduced in a powder form and the quantity used is generally within the range 5–10 % of dry mass.

The dimensions of the fire retardant particles affect their effectiveness and the amount added, especially for the fire retardation of polymers [21, 192, 193]. Commonly used inert fillers for composite materials are silica, calcium carbonate, talc, glass fibre and other. They improve the fire retardancy and decrease smoke yield by mechanism of fuel dilution in the solid phase [194].

10.3.4.3 Paper and Paper Products

Flame-retardants recommended for paper and paper products have closely paralleled those suggested for other forms of cellulose, particularly wood. The most commonly used materials are ammonium sulfate and ammonium phosphates, with or without boric acid, but a large number of more sophisticated retardants have been suggested for various specialty applications [167].

There are several modes of adding flame-retardants to paper products, depending on three parameter: (a) the solubility of the compounds, (b) the paper product involved, and (c) the cost considerations.

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