FIRE RESISTANCE OF POLYMERS

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ABSTRACT

Polymers are well known as easily flammable. On the other hand, the use of polymers – as such and also as constituents of composites and coatings – is growing rapidly. We discuss polymers and polymer-based materials from the point of view of flammability. We also note more briefly the effects of fires on humans. Some measures towards limiting that flammability are discussed.

Keywords: *polymer flammability; polymeric composites; fire prevention; flame retardants*

INTRODUCTION AND SCOPE

The use of polymers and polymer-based materials (PBMs) is growing fairly rapidly. Traditional materials based on metals or ceramics do not burn easily – or at all. PBMs are now used more and more for several reasons. One reason is their relatively low prices, including low costs of processing. Another reason is that their densities are lower than those of metals and ceramics. *An all composite airplane is lighter than a plane with a metal body, therefore it can fly further on a given amount of fuel*. The increasing use of PBMs behooves us to apply to them standard methods of fire prevention - or better, to develop new ones.

The nature of PBMs used by humans is changing. In the past we used mostly synthetic polymers. Now wood is becoming a more and more important natural PBM. The need for preservation of the environment shifts the use of polymers from man-made to natural ones [1, 2].

There is also a large variety of other products which used to be obtained from petroleum - but now equivalent products can be produced instead from biomass feedstocks. e.g. lubricants, textiles, adhesives, thickeners, stabilizers and a range of celullosics. In contrast to PBMs, such materials can be biodegradable.

In 2015, in the U.S.A., 501 structure fires caused 2685 deaths and 10.3 billion dollars in direct property damage. Fires in Australia in 2019 destroyed about 1,000 homes and burned more than 12 million acres; [one acre = 4047 m^2]. The same year there were many fires in Russia, in particular in Siberia, even close to cities such as Novosibirsk and Krasnoyarsk, where air quality plummeted [2].

We shall discuss effects of fires on inanimate objects – as well as fire toxicity of polymers which can even result in human fatalities. We shall also discuss fire retardation and mitigation. The field of this review has been claimed by several disciplines: Materials Science and Engineering, Thermal Physics, Rheology, also Environmental Science all meet here – providing a region of overlap.

BEHAVIOR OF POLYMERIC MATERIALS IN THE PRESENCE OF FIRES

An overwhelming majority of polymers in use are organic – and they are flammable – while inorganic polymers exist also [3]. Common electronic devices including cell phones typically contain lithium ion batteries. Such batteries contain organic solvents and lithium salt. Battery fires are typically a result of heat generated due to a short circuit within one or more of the battery cells. Water together with heat cause the thermal dissociation of $LiPF_6$ and the resulting Lewis acid PF_5 'attacks' the solvent molecules, The combustion of large amounts of active free radicals is a process called "thermal runaway". The U.S. Federal Aviation Administration has reported that one 'incident' involving lithium ion batteries occurs in the U.S.A. every 10 days – either on airplanes or at airports [4]. For instance, in November 2017 the lithium ion battery of a camera exploded at Orlando International Airport at a security checkpoint - which caused a terminal to be evacuated [4].

Polymers and PBMs appear in various forms, such as bulk objects, coatings, foams and fibers. Dealing with them, one has to apply a multi-scale approach [5]. As expected, the surface to volume ratio is important. Foams burn easily, as do films and fiber structures. Coatings are 'protected' from the substrate side. Bulk objects flammability is approximately inversely proportional to the surface to volume ratio.

Horizontal and vertical fire spreading velocities are not the same. It has been demonstrated already in 1988 by Babrauskas and his colleagues [6] that fires spread vertically faster. One possible explanation is that oxygen is needed to sustain fire, warm air goes up, and cooler air with 'fresh' unused oxygen arrives from below. Testers have been developed which can be operated in either horizontal or vertical positions.

The statement that fire causes thermal decomposition of polymers deserves a more detailed consideration. Beyler and Hirschler [7] note that one should distinguish thermal *decomposition* from thermal *degradation*. ASTM International in West Conshohocken, Pennsylvania, U.S.A. (previously American Society for Testing and Materials) provides definitions in this respect. Thermal decomposition is "a process of extensive chemical species change caused by heat". Thermal degradation is "a process whereby the application of heat or elevated temperature on a material, product, or assembly causes a loss of physical, mechanical, or electrical properties".

Levchik[8] discusses four modes of decomposition:
1) random chain scission, in which the polymer backbone is randomly split into smaller fragments;
2) chain-end scission, where depolymerization begins at the chain ends;
3) elimination of pendant groups – but without breaking of the backbone; and

4) cross-linking. This might appear even mutually contradictory, but chain scission and cross-linking can take place simultaneously at different locations.

Everyday experience tells us that a polymer 'left alone' at room temperature will not burn. A source of heat is a typical prompting factor. With the fire already burning, the increased amount of heat available causes new decomposition reactions in the solid polymer—and thus more fuel to burn—literally and figuratively.

It is worth noting that it is not the polymer itself that burns, but rather the combustible gases resulting from a decomposition (pyrolysis) reaction which occurs when heat is applied. The gases diffuse and mix with the oxygen [9] - as illustrated in Figure 1.

FLAMMABILITY TESTING

How do we characterize flammability of polymers and PBMs? Several methods are in use. First, however, we need to discuss creation and use of the standards. There exists the International Standards Organization (ISO) based in Geneva. For example, Deutsches Institut für Normung (DIN) based in Berlin is a representative in ISO for Germany. There are also some standards developed for internal use within a single country. Well known among them are U.S. standards of ASTM International (American Society for Testing and Materials, not American Society for Testing Materials), in existence since 1898.

The *cone calorimeter* test is a bench-scale (medium-sized) test developed in the U.S.A. which quickly gained popularity in the academic community as well as for standardization purposes (e.g., ISO 5660-1, ASTM E-1354); We show this in Figure 2.

This type of calorimeter has an important advantage: it makes possible reasonable prediction of large-scale test results. One determines consumption of oxygen from a burning sample 100×100 mm in area; the thickness varies - up to 50 mm. One uses the oxygen consumption data to calculate the heat produced. There is a constant heat flux from a conical-shaped irradiation source (hence obviously the test name). One believes that one can simulate a variety of fire scenarios. One uses a small sparking igniter, causing ignition of gases evolved from the heated specimen. One can determine time to ignition, weight loss and smoke generation rate. One can monitor formation of carbon monoxide, carbon dioxide, and also formation of corrosive gases such as HCl and/or HBr.

Another often used laboratory test consists in the determination of the *limiting oxygen index* (LOI) shown in Figure 3.
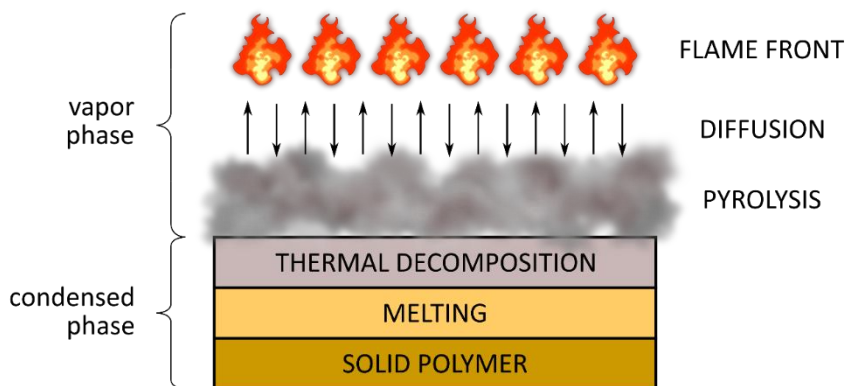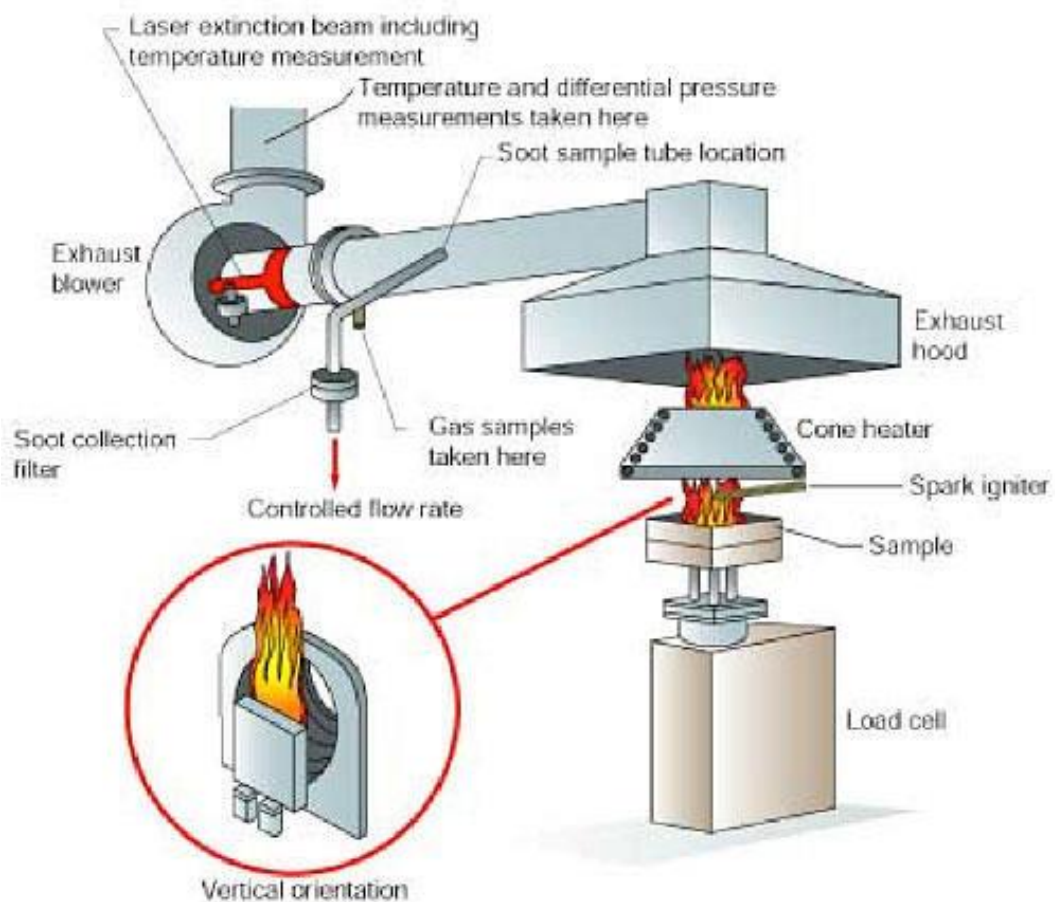

Figure 1. Combustion of polymers.
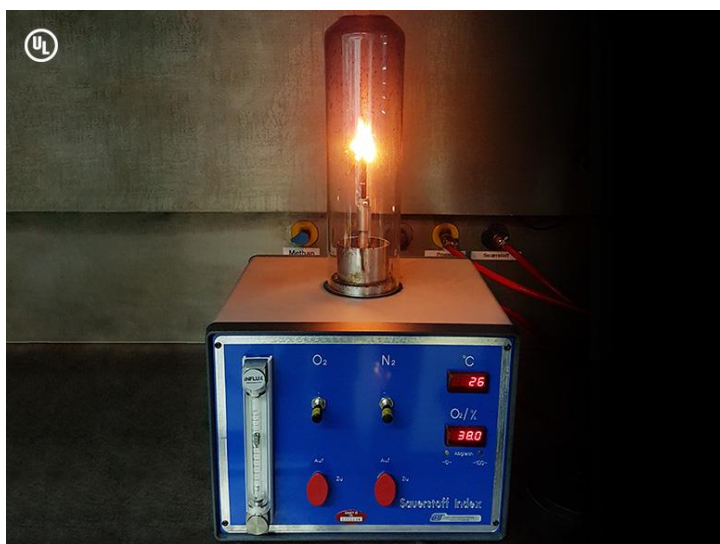
Figure 2. The cone calorimeter.

Figure 3. Limiting oxygen index determination.

One works typically with bars of approximately $100 \times 65 \times 3$ mm – while the specimen size and shape are not strictly defined. LOI is included in some national and international standards, in particular ASTM D2863 and ISO 4589. The specimen is placed vertically in a glass chimney and is held from the bottom. The chimney is purged continuously with a mixture of nitrogen and oxygen. The flame of a Bunsen burner is applied to the top of the specimen until the entire surface is ignited. If the specimen did not ignite after 30 s, the concentration of oxygen is increased. Ideally, the specimen should show stable candlelike combustion. If the specimen continues burning more than 3 minutes after removal of the ignition source or if more than 5 cm of the length of the sample is consumed, a new specimen should be installed and tested at a lower oxygen concentration. The LOI value is the limiting concentration of oxygen at which the sample tested self-extinguishes in less than 3 min with less than 5 cm of the material consumed. That is:

$$LOI = 100[O_2]/([O_2] + [N_2]) \qquad (1)$$

Here the values in square brackets are concentrations per unit volume. Materials with a LOI lower than 21 are considered combustible while those with an index higher than 21 are self-extinguishing. Clearly the higher the LOI value, the better the flame retardancy of a polymer. The LOI test does not represent a real fire scenario, but it is good as a screening tool because it gives a numerical value - instead of discrete classification numbers (sometimes still in use).

An organization called Underwriters Laboratories (UL) based in Northbrook, Illinois, U.S.A., tries provide among others some guidance to polymer flammability. Discussing some flammability monitoring, they say: "The performance level of a material determined by these methods shall not be assumed to correlate with its performance in end-use application. The actual response to heat and flame of materials depends upon the size and form, and also on the end-use of the product using the material. Assessment of other important characteristics in the end-use application includes, but is not limited to, factors such as ease of ignition, burning rate, flame spread, fuel contribution,

intensity of burning, and products of combustion". These statements pertain to polymers, while UL says also: "If found to be appropriate, the requirements are applied to other nonmetallic materials".

Since UL standards are so widely used, we discuss here in some detail the UL 94, the Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances. It comprises five test programs for characterization of different plastic materials and their properties. Two tests are designed to measure horizontal burn: UL 94 HBF for foamed materials and UL 94 HB for other materials. A slow horizontal burn can be considered as self-extinguishing. Three tests determine flammability characteristics when a vertical flame is applied. The first, UL 94 V, measures the material tendency either to extinguish or to spread the flame once the specimen has been ignited (time of burning and afterglow and also dripping behavior). When the material is not capable to remain in a vertical position, the second one, UL 94 VTM (Thin Material test), may be applied. The condition of the test is similar to the previous one, but an additional handle for the specimen is mounted, and flame duration is shorter. The most rigorous test is UL 94 5V, which evaluates time of burning and afterglow, but also a hole formation. The burning or afterglow has to stop within 60 seconds after 5th flame [10-12].

The other group of UL tests pertain to the ignition resistance of the plastic to electrical ignition sources. They are described in UL 746A Standard for Safety Polymeric Materials – Short Term Property Evaluations. Hot Wire Ignition (HWI) test is used to characterize electrical insulation materials. On the basis of the test, the materials are assigned to one of six Performance Level Classes (PLCs). High-current (or High-amp) Arc Ignition (HAI) and High-Voltage arc Tracking Rate (HVTR) are the other basic tests used to determine polymer resistance to ignition from electrical sources [10, 13].

There are also some standards for special situations. There is a solar furnace at the

Plataforma Solar de Almeria in Tabernas, Province of Almeria, Spain. A schematic of its operation is shown in Figure 4, and a photograph of the installation is shown in Figure 5.

The platform can intensify the natural solar beam of 25 cm diameter with energy density over 300 W/cm^2; and it can heat up specimens to temperatures above 2000°C [14]. A team consisting of Plataforma researchers plus several based in Kaunas, Lithuania, plus two of the present authors [15] studied fire doors subjected to the solar furnace heat. There were door slabs typically used for the purpose as well as those modified with a mixture of liquid sodium silicate including montmorillonite as thermal insulation. The slabs were examined under thermal shock conditions. In Figure 6 we show (a) a sample imitating a fire door element made of stone wool after solar irradiation and (b) a cross section of the tested sample (thickness of 100 mm) showing the depth influenced by the pyrolysis process of the polymeric binder in the sample at 950°C during 1 hour.

X-ray diffraction, thermogravimetry, differential scanning calorimetry, scanning electron microscopy, Fourier transform infrared spectroscopy, and thermal conductivity measurements were performed on the sample door. N_2 adsorption/desorption isotherms were determined. X-ray diffraction patterns show that during the thermal shock at 950°C, xonotlite in the slabs is converted to wollastonite. Specific surface areas of xonotlite slabs decrease due to release of crystalline water molecules. It is possible to maintain temperatures at the back door not exceeding 70°C while the front door is subjected to 950°C for 1-h time periods. This time period and the temperature are prescribed by the standard – in this case well complied with [15]. The standard requires temperatures not exceeding 140°C at the back door.
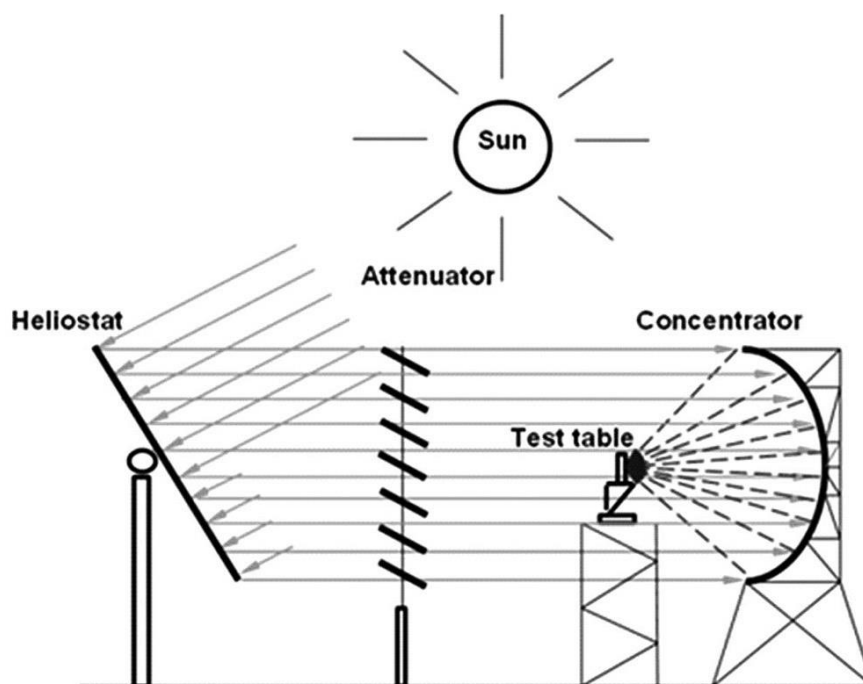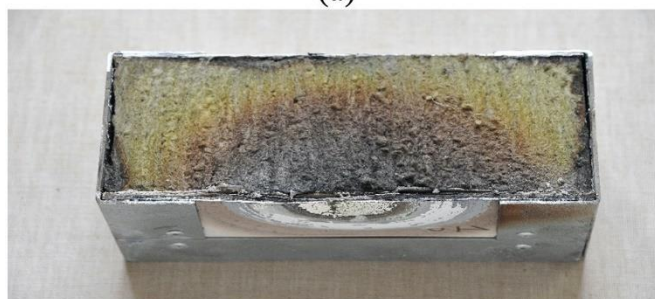

Figure 4. The schematic of operation of the SF60 Solar Furnace at the Plataforma Solar de Almeria in Tabernas, Almeria, Spain.

Figure 5. A photograph of the Plataforma.

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Figure 6.   A door imitation; (description in text)

BEHAVIOR OF HUMANS IN THE PRESENCE OF FIRES

The worst effect of fire is suffocation of the person from the smoke produced by burning matter. First, the smoke can restrict oxygen flow into the body. Second, the smoke contains poisons - typically lethal.

Even if humans will not die, the heat from the fire will cause significant damage to human bodies. One can simply say that the human body consists of soft and hard tissues. Of course, fire will have a dramatic effect on both kinds of tissues. The fire will cause the soft tissues to contract; this causes the skin to tear while the body fat shrinks, and the muscles shrink too. The internal organs will shrink as well. The muscles contract due to burning and this causes the joints to flex. Then burned bodies take what is called a pugilistic (boxer) pose. This pose is seen particular in bodies recovered from the ancient Roman (now Italian) city of Pompei. The volcano Vesuvius eruption in year 79 of our era destroyed soft tissues of the humans – while the hard tissues remained. Stone-made buildings remained as well - covered for a long time with ash. Now a worldwide tourist attraction, Pompei is a United Nations Educational, Scientific and Cultural Organization (UNESCO) Heritage site.

FIRE RETARDATION IN POLYMERS AND PBMS

Flame retardants (FRs) may be incorporated into polymers in order to reduce their flammability. FRs interrupt the combustion process by inhibiting the inflammatory process and/or reducing pyrolysis rate and oxidation reactions. FRs are applied as surface coatings or else added to the bulk of the polymer. FRs added to the bulk belong to one of two groups: additives and reactive FRs. Additives do not react with the polymer matrix during formulation process; they do so only at elevated temperatures—when the fire starts. Reactive flame retardants are constituents of polymer chains, that are parts of the polymer itself. Monomers, precursors and curing agents fall into the latter category [9, 16, 17].

Due to incorporation into the polymer matrix, they are more homogeneously distributed in the polymer than FR additives and also less prone to migration. However, their usage is usually more expensive and they are less versatile than FR additives; thus the latter are more popular [9].

Mechanisms of fire retardancy

The interruption of fire may be done in various ways, according to physical or chemical mechanisms [9, 17, 18].

Physical:
- heat sink: endothermic decomposition of FR or endothermic reactions promotion; the result is decreasing temperature of the polymer and thus hindering flame propagation;
- inert gas evolution: releasing of inert gases during FRs decomposition (e.g. H_2O, CO_2, NH_3, hydrogen halides) dilutes combustible gas in the proximity of the polymer surface and thus impedes ignition and flame development;
- protective solid layer: FRs coatings form impermeable layer on the polymer surface which limits heat and oxygen transfer to the polymer and combustible gases from polymer to vapor phase.

Chemical:
- free radical scavenging, that is interrupting radical reactions which are responsible for flame propagation— what slows down flame propagation or even stops char formation, that is promoting formation of a char layer on the polymer surface; then the surface is not susceptible to pyrolysis—preventing the release of combustible gases;
- intumescence: heated materials start to swell and expand, forming a protective layer;
- acceleration of polymer decomposition – promoting polymer melting, so that the molten zone separates the rest of the polymer from the flame zone; (Think about the behavior of a candle from which the wick is removed.)

Examples of compound groups used as flame retardants - that show different mechanisms of flame retardancy - are collected in Table 1.

Table 1. Examples of flame retardants with specific modes of action [9, 17, 19].

Flame retardancy mechanism	Flame retardant example
Physical	
Heat sink	mineral fillers, zinc borates, halogen-based compounds, nitrogen-based compounds
Inert gas evolving	mineral fillers, zinc borates, nitrogen-based compounds
Protective solid layer formation	mineral fillers, zinc borates, phosphorus-based compounds, silicon-based compound
Chemical	
Free radical scavenging	halogen-based compounds, phosphorus-based compounds
Char formation	zinc borates, phosphorus-based compounds
Intumescence	phosphorus-based compounds, expandable graphite

Fire retardants

Halogen-based compounds

Historically, halogen containing organic compounds were the first fire retardants successfully used in synthetic polymers. They were introduced in 1929 [20]. For years, it was the most popular group of polymer flame retardants due to their ease of use, which means that there is a wide range of compounds which can be chosen regarding polymer type and its thermal stability required for the application selected. The other advantages are low cost and industry experience with these FRs [9].

Halogenated FRs inhibit flame propagation in gas phase—working as free radical scavengers. They generate hydrogen halides or halogen radicals (which turn into hydrogen halides reacting with the polymer matrix). Subsequently, hydrogen halides react with free radicals, such as H• or OH•; the radicals are the main species responsible for propagation of combustion. Much less reactive halogen radicals are formed in these reactions. Moreover, halogen-based compounds act also as heat sinks—reducing the heat released during combustion of the gases from polymer degradation. Some of the halogenated FRs can also catalyze polymer oxidation, thus leading to formation of protective char [9]. Gases from combustion of materials containing halogenated FRs are often smoky and full of incomplete combustion products, such as halogen hydrides and organic halogen compounds (e.g. dioxins). This is a major drawback of their use [19].

Since the 1930s, polychlorinated biphenols (PCBs) (Figure 6) had been the most widely used halogenated FRs, but due to their toxicity [21] and environmental persistence they were banned in 1979 in the U.S.A. and in 2001 by the Stockholm Convention on Persistent Organic Pollutants, signed by 184 parties [22]. In 1970s PCBs were replaced by brominated flame retardants [20]. The natural replacement for PCBs seemed to be polybrominated biphenols (PBBs), with the same biphenyl moiety, in which chlorine atoms were replaced by bromine (Fig. 2). In 1973 PBBs were accidentally mixed into animal feed in the State of Michigan, U.S.A., which caused animal poisoning, and 9 million people exposure to toxic food. Subsequent detailed studies revealed that PBBs health effects are practically the same as PCBs and they are not produced any more [23]. The most popular in the 1990s were polybrominated diphenyl ethers (PBDEs) (Fig. 2), that have been manufactured as FRs since 1965 [20]. They had a tendency to accumulate, but for a long time they were considered nontoxic. However, later studies showed some adverse health effects, like hormone-disrupting activity or negative impact on sexual and brain development [20]. Thus, use of all major classes of PBDE (tetra-, penta-, hexa-, hepta-, octa- and deca-PBDEs) are currently banned or strictly controlled by Stockholm Convention [22] or other regulations (.EU., U.S.A. and other countries) [24]. Another widely used

brominated FR which was put under restriction is hexabromocyclododecane (HBCD) (Fig. 7), which is now allowed to be used only in expanded or extruded polystyrene in buildings [22]. As can be seen from the above examples, the phased-out compounds are often replaced by

new compounds with similar structure and *unknown impact* on health and environment. More profound research should be conducted to assess the safety of newly introduced flame retardants.
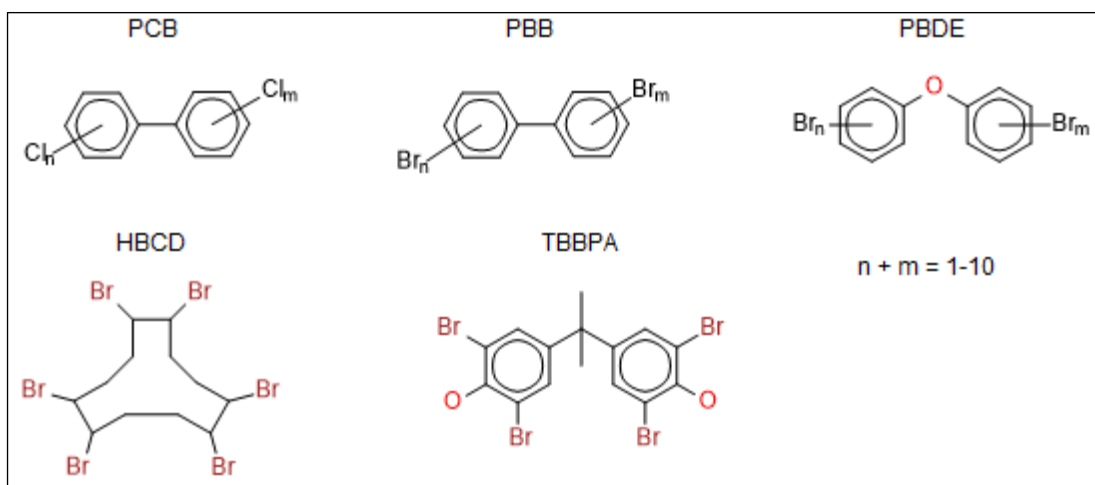

Figure 7. Examples of halogenated flame retardants: polychlorinated biphenols (PCBs), polybrominated biphenols (PBBs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA).

In 2016, halogenated FRs still accounted for 22% of global FRs production, of which 17% are brominated FRs and 5% are chlorinated [25].

The most widely used halogenated flame retardant at this time is tetrabromobisphenol A (TBBPA) (Fig. 6). In contrast to the abovementioned FRs, it is not an additive but a reactive component. It is used mainly for the synthesis of epoxy resins [17]. The most common type of epoxy resins is diglycidyl ether of bisphenol A (DGEBA) [26]. TBBPA is used as a partial replacement of bisphenol A during synthesis of epoxy resins—with enhanced flame retardancy, especially for use in printed circuit boards [17, 26]. Another reactive halogenated FR is vinyl bromide used for synthesis of a copolymer with methyl methacrylate (MMA) [16]. Like all reactive FRs, also halogenated ones are less prone to leaching than additive FRs because they are constituents of the polymer backbone. Thus, they are considered more environmentally safe. However, there is an increasing consumer pressure on complete removal of halogenated compounds from polymers [9].

In order to enhance fire retardant activity of halogenated compounds, so-called synergists are added. Among them, the most widely used is antimony trioxide (Sb_2O_3). However, study on rats proved that antimony trioxide might cause cancer [27] and it was classified by the European Union as suspected to be cancerogenic [28]. Therefore, other compounds are used as replacements, such as zinc borates [29].

Mineral fillers and other inorganic compounds
The most common replacement for halogenated flame retardants is aluminum hydroxide $Al(OH)_3$, also known as aluminum trihydrate (ATH). It accounted for almost 40% of the total volume of non-halogenated FRs sold in 2019 [30]. ATH is one representative of mineral fillers, which can serve as nontoxic and the least expensive FRs. The other benefit is their white or light color, nonvolatility and easy handling [31, 32]. The main drawback is high loading which is required to achieve proper fire retardancy; typical ATH filling level is 55-65 wt.% - which can lead to deterioration of physicochemical and

mechanical properties of polymeric materials and also complicate processing [33, 34]. Typically, in order to lower the loading, mixtures of fire retardants are used. Beside ATH, also other metal hydroxides are used, mainly magnesium hydroxide $Mg(OH)_2$ (magnesium dihydrate - MDH) and also calcium hydroxide $Ca(OH)_2$ [35].

Upon heating, metal hydroxides decompose endothermically, releasing water. Metal hydroxide decomposition reaction upon heating is shown in Eq. 2 using an example of ATH. Because the decomposition absorbs energy, the polymer cools down. Moreover, water molecules dilute combustible gases and metal oxide (e.g. alumina, Al_2O_3) forms as a protective layer on the polymer surface. All these three effects lead to fire extinguishing. They are also smoke suppressant [9, 17].

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \qquad (2)$$
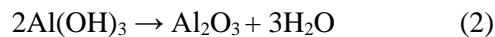
In order to effectively work as FRs, metal hydroxides need to decompose at a temperature higher than the polymer processing temperature and close to the polymer decomposition temperature. ATH is stable up to 190°C, which is lower than processing temperature of many commonly used polymers, such as poly(ethylene terephthalate) (PET), polycarbonate (PC), polypropylene (PP), polyamide (PA) or poly(butylene terephthalate) (PBT) [31, 32]. ATH application is limited to the polymers obtained at lower temperatures such as ethylene vinyl acetate (EVA), low density polyethylene (LDPE) or epoxies and thermoset polyesters [17, 3]. For other, magnesium or calcium hydroxides can be used since they decompose in the temperatures above 340°C [35, 36].

Another endothermically decomposing mineral fillers are carbonates, mainly magnesium hydroxycarbonate, in the form of natural or synthetic hydromagnesite [36-38], and huntite-hydromagnesite (HH) – a naturally occurred mixed mineral [36, 37, 39-41]. Formulae and some properties of these compounds are gathered in Table 2.

Hydroxycarbonates release water when decomposing, but also carbon dioxide at higher temperatures. Both reactions are endothermic and provide inert gases which dilute combustible gases. Hydroxycarbonates can serve as an alternative to ATH or MDH, since they decompose in the wider range of temperatures; see Table 2. Huntite, which is not hydroxycarbonate, because of the lack of water or hydroxyl moiety, releases only CO_2 when decomposes. Its fire suppressant performance is worse, but its decomposition temperature is very high, so it is used when excellent thermal stability of polymer is desired [9]. Hydromagnesite-huntite FRs are applied when processing temperature is too high for ATH and when MDH is too expensive, especially for production of cables and wires [9].

To improve polymer processing and adhesion of hydromagnesite and huntite FRs to polymers, various techniques have been applied, such as silanization of hydromagnesite-huntite [42] or hydromagnesite coating with stearic acid [38, 43]. Stearic acid was added to increase filler–matrix interactions and filler dispersion in the matrix.

Borates are another group of inorganic FRs. Among them the most popular are zinc borates, but also calcium borates, in the form of mineral colemanite, were tested [44-47]. Zinc borates are widely used solely or in a combination with other FRs, mainly as a replacement of antimony trioxide in halogenated FRs and also with hydroxides or carbonates [18, 29]. Depending on synthesis condition zinc borates with different mole ratios of $ZnO:B_2O_3:H_2O$ are obtained. Apart from composition, they also significantly differ in their decomposition temperatures [29]. Examples are provided in Table 2.

As mineral fillers, zinc borates decompose endothermically releasing water, but also boric acid and boron oxide. Thus, they act as heat sink and also dilute combustible gases. Boron oxide forms vitreous layer, which protects polymer. Moreover, boric acid causes dehydration of polymers that contain oxygen. It results with char formation, which provide additional protection for polymer. Zinc borates work also as smoke and afterglow suppressant [9, 17, 28].

Table 2. Properties of some common mineral and inorganic fillers [17, 19, 29, 36, 44, 46].

Name	Formula	Decomposition temperature [°C]	ΔH [kJ/g] [a]
aluminum hydroxide (ATH)	$Al(OH)_3$	190-350	1050-1300
magnesium hydroxide (MDH)	$Mg(OH)_2$	340-450	1300-1450
calcium hydroxide	$Ca(OH)_2$	430-450	1150
Hydromagnesite	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ or $5MgO \cdot 4CO_2 \cdot 5H_2O$	200-250 380-450 510-550	800-1300
Huntite	$CaCO_3 \cdot 3MgCO_3$	400	980
Ultracarb® (hydromagnesite/huntite 60/40)	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ or $5MgO \cdot 4CO_2 \cdot 5H_2O$ and $CaCO_3 \cdot 3MgCO_3$	200-250 350-430 540-600 725-780	1172
Firebrake®ZB	$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$	290	503
Firebrake®415	$4ZnO \cdot B_2O_3 \cdot H_2O$	415	
Firebrake®500	$2ZnO \cdot 3B_2O_3$	500	
Colemanite	$2CaO \cdot B_2O_3 \cdot 5H_2O$	360-400 400-720	

[a] ΔH is the enthalpy of combustion

Inorganic FRs which exhibit exceptionally good smoke suppressing properties are zinc stannate ($ZnSnO_3$) and zinc hydroxystannate ($ZnSnO_3 \cdot 3H_2O$). They have been used instead of antimony trioxide in halogen-containing polymers and also as a partial replacement of ATH and MDH in halogen-free systems. They are commercially used in plastics, rubbers and paint formulations [18, 34].

There is also a wide range of other inorganic fire retardants, which however have not found commercial application yet. Among them predominate various metal oxides and complexes [48].

Mineral fillers and inorganic compounds can work only as additive FRs, not reactive ones, since it is hard to form stable bonds between inorganic moiety and organic monomers or polymers [18].

Phosphorus-based compounds....

The third most popular group of FRs are organophosphorus compounds, which gained 18% of the market share in 2016 [25]. However,

not only organic forms of phosphor retard fires but also inorganic phosphates and even red elemental phosphorus [8, 49]. Inorganic polyphosphates are a key ingredient of intumescent fire retardant systems - which will be discussed in the next section.

Phosphorus-based FRs can act in condensed and in vapor phase, which depends on polymer and FR type, but also on other additives present in a polymeric system. That is why phosphorus-based FRs are formulated individually for every polymeric material. In condensed phase, they form phosphoric and polyphosphoric acids or their anhydride which cause polymer dehydration and, as a result, polymer charring. This mode of action is highly effective in oxygen- or nitrogen-containing polymer. In polymers without these elements, co-additives, such as polyols are added to promote char formation. Moreover, phosphoric acids evolved during FRs decomposition can form a vitreous or liquid protective layer on the surface of a condensed phase. In vapor phase, phosphorus-based FRs act as free radical scavengers. Upon heating, they form volatile phosphorus-based

radicals, which have proved to be much more effective than chlorine and bromine ones [9, 17, 18, 49].

Red phosphorus is indeed red, a nontoxic powder, stable up to 450°C. It enhances fire resistance of polymers even if added in small amounts (< 10%). However, it imparts its color to the polymer. More importantly, it reacts with moisture and oxygen, producing highly toxic phosphine (PH_3). To avoid this process, red phosphorus can be encapsulated in resins or used together with metal salts or oxides (e.g. CuO, ZnO, $AgNO_3$) which react with phosphine, transforming it into phosphoric acid [9, 17, 49].

Organic phosphorus FRs can be additives or monomers used with other comonomers to obtain polymers. Additive FRs containing phosphorus belong to one of three groups: phosphinates, phosphonates and phosphate esters, which differ in the number of oxygen atoms bonded to a phosphorus atom. Examples of fillers are shown in Fig. 8.
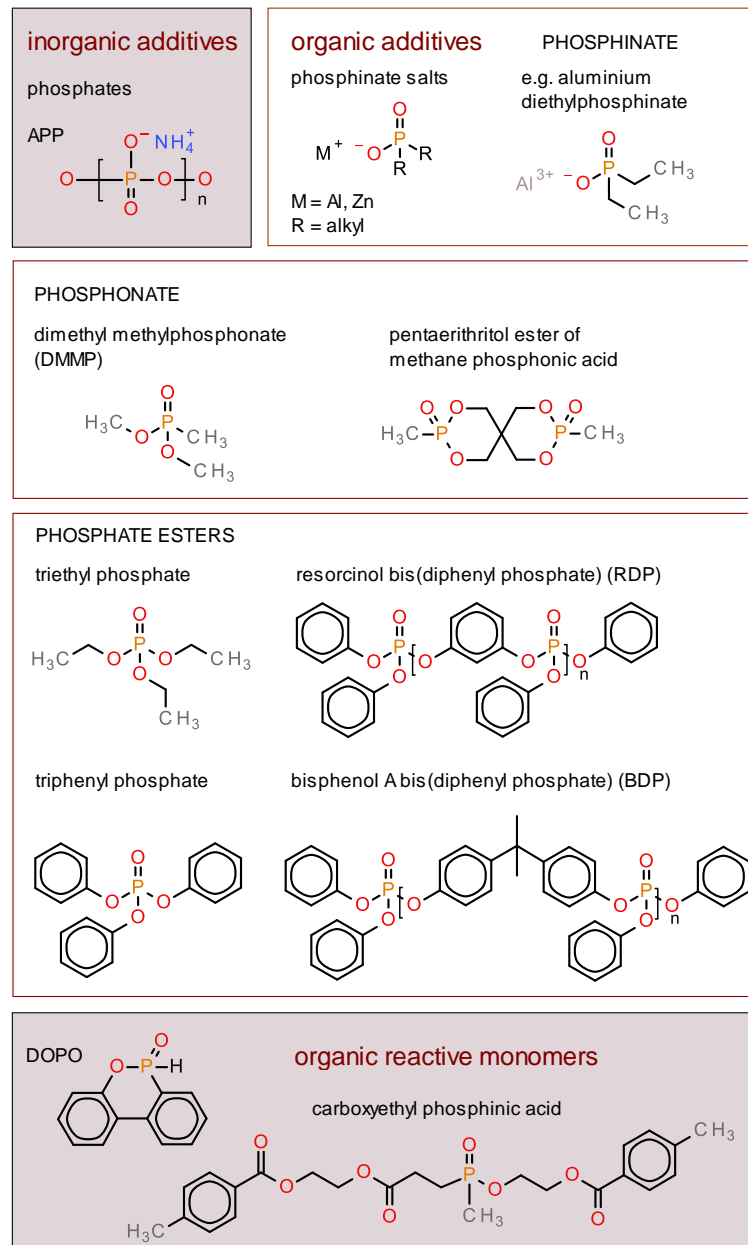

Figure 8. Chemical structures of phosphorus-based flame retardants.

As mentioned in the previous section, additive FRs can cause deterioration of mechanical properties. They also tend to migrate in the polymeric material and evolve as volatile organic compounds (VOCs). Many strategies have been proposed for immobilization of phosphorus-based FRs in the polymer matrix.

An interesting approach was proposed by Xiao-Lin Qi and coworkers in Madrid and Guagzhou [50] who obtained porous metal−organic framework (MOF) particles and created multifunctional interfaces between the fire retardant molecules and the polymer. A MOF were treated with DMMP and then embedded into widely used unsaturated polyesters. One thus obtains composites with improved processability, flame retardancy, and apparently better mechanical properties.

Fewer compounds serve as reactive FRs. In commercial use are DOPO (dihydrooxa-phosphaphenanthrene oxide) and carboxyethyl phosphinic acid (Fig. 8). These two are mainly used in poly(ethylene terephthalate) (PET) or polyamide (PA) fibers, polyurethane (PU) foams and printed circuit boards based on epoxy resins [9,17,49]. More structures have been studied, but not commercialized yet, such as cyclic phosphazenes and linear phosphazenes [9]. A wide range of phosphorus-containing curing agents for epoxy resins were tested - Schiff bases, anhydrides, aliphatic amines, and imidazoles [51].

Sometimes FRs are created with specific polymers in mind. Realinho and her colleagues [52] developed phosphorus-based FRs for acrylonitrile– butadiene–styrene (ABS) parts.

A still different popular class of polymers are poly(methyl methacrylates) (PMMAs). They can be made from phosphorus containing monomers - while fire retardation properties of such polymers have been studied by Cochez and coworkers [52]. No monomer molecules were found during the thermal degradation – this in contrast to ordinary PMMA. Methyl methacrylate (MMA) can be also copolymerized with various vinyl phosphorus-based monomers.

Polymers so obtained exhibit good charring properties under fire conditions [53].

Intumescent systems

Intumescent systems form a protective carbon foam under fire condition. Their name derives from the word intumesce, which means swell up when exposed to heat.

An intumescent system typically consists of three components:
- carbon source,
- acid catalyst,
- blowing agent.

The acid catalyst reacts with carbon source. It results with highly crosslinked char, which is thermally stable. The blowing agent releases gases when heated. Thus, it transforms char into carbon foam, which has better insulation properties than non-foamed char [18].

The carbon source can be part of the intumescent system or it can be polymer itself. The most popular external carbon source is pentaerythritol. Usually carbohydrates are used, but it can be also phenol-formaldehyde resins. These compounds are dehydrated by an acid catalyst. As an acid typically serves ammonium polyphosphate (APP) [54] mentioned shown in the previous section (Figure 8). Also, other acid salts and inorganic acids can be used. Melamine is usually used as a foaming agent. Other examples are guanidine urea and chlorinated alkanes.

In order to avoid problems with suitable proportion of all three components - which will provide desired fire-retardant properties to the material - intumescent systems composed only of one compound were proposed. In such systems, one compound plays all three roles simultaneously. One example is expandable graphite. It is a carbon source, and therefore it does not need acid catalyst to form a char. Instead, graphite expands when gases from between graphite layers are released [55]. An interesting example is deoxyribose nucleic acid (DNA), which proved to be a very efficient and universal flame retardant for a broad range of polymers (EVA, PP, ABS, PET, and PA-6). A DNA segment consists of phosphate moiety

which is an acid source, deoxyribose (carbohydrate) as a carbonizing agent and nitrogen-containing base which is blowing agent [56]. If only DNA becomes more available, it may serve as a versatile, nontoxic and effective FR.

APP was usually combined with pentaerythritol, but this carbon source tends to migrate during processing. It was successfully replaced by polyamide 6 (PA-6). Moreover, PA-6 can be used to create PA-6 clay nanocomposite, which further enhanced fire resistance of the material [17]. Also, triazines and their derivatives can act as a charring agent with APP [57].

As we can see from the above example, polymers can be a part of intumescent systems if only each chain contains suitable groups. Polyamide 6 can be used with melamine polyphosphate. The polymer serves as carbon source and melamine polyphosphate as both an acid catalyst and a blowing agent [9]. Rigid polyurethane foams can be prepared using melamine-formaldehyde resin, which together with additives mentioned earlier, namely APP and dimethyl methylphosphonate (DMMP), provide excellent flame-retardant performance [58].

Intumescent FRs were first used in coatings and paints. Such systems protect underlying material from fire and thermal damage. It is common solution for construction elements made of steel and wood, but also for fabrics and products made of rubber and plastic [17, 18, 49]. They are also used in cables and wires [49].

Beside their great insulation properties, intumescent systems lower smoke and toxic gases emission and exhibit anti-dripping properties. However, they have also some limitations. They absorb or even solubilize in water, which may cause their leaching from polymeric material. Their thermal stability is poor and they are expensive [9, 59].

In order to enhance the performance of FRs, numerous synergy strategies have been studied. Among the materials considered are metal borides, nitrides or carbides. Also, mineral fillers were examined such as clay, zeolite, talc, MnO_2, CaO, $CaO \cdot Ca(OH)_2$ [44], or borates [29, 46]. Much attention gain nanofillers, such as nanoclay mentioned above and layered silicates [9].

In order to lower the price and increase their availability, cheaper replacements for conventional components of intumescent systems are sought. Jung at al. [60] proposed a FR based on chicken feathers loaded with ethylenediamine phosphate - for manufacturing of polypropylene (PP) with enhanced fire resistance. Use of the waste product - chicken feathers - significantly reduces the cost of such a system.
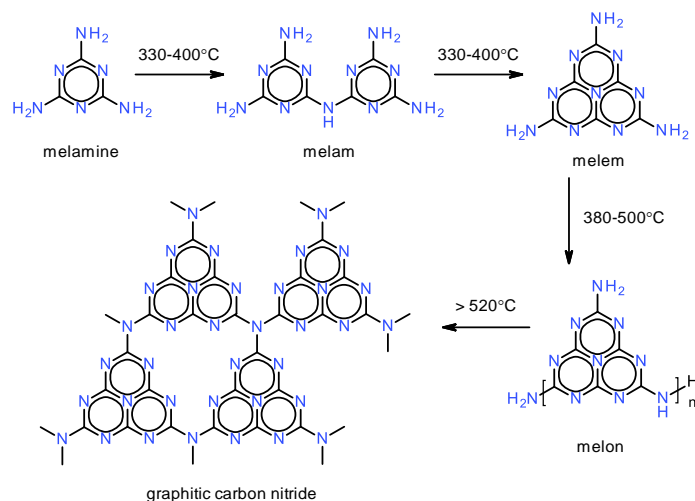

Figure 9. Decomposition pathway of melamine upon heating [61].

Nitrogen-based compounds

Melamine, which is a common component of the intumescent systems, is the main representative of nitrogen-based FRs; (See Figure 9). Other such compounds are melamine derivatives and some heterocyclic compounds. This group comprises compounds which are environmentally benign and upon heating do not release significant amount of smoke or toxic gases. However, they are not as effective alone as FRs described in previous sections. They are often combined with other FRs, mainly in intumescent systems [9, 17].

Melamine has a melting point of 345°C. When heated above this temperature, two processes occur. At 350°C, melamine endothermically sublimates, thus acting as a 'heat sink'. At higher temperatures it decomposes, releasing ammonia molecules - which dilute combustible gases. Thermally stable condensates are formed in this process: melam and melem. Above 380°C melem transforms into polymeric melon. Above 520°C further condensation proceeds (Fig. 9). Graphitic carbon nitride (g-C_3N_4) is formed - which shows excellent chemical and thermal stability [61]. Such carbon nitride was also tested alone as a component of a nanocomposite. It improved thermal and mechanical properties of sodium alginate nanocomposite films [62].

Nitrogen-phosphorus-based compounds

Another class of FRs are nitrogen-phosphorus-based compounds which are more thermally stable and generate less toxic smoke than phosphorus FRs. Vothi and coworkers [63] prepared FRs based on phosphonamidite and bisphosphoramidate. The former act mainly in a gas phase (via active radicals), while the latter act in a condensed phase (charring behavior).

Silicon-based compounds

Another group of environment-friendly FRs are silicon-based compounds, both organic and inorganic, such as silicones, silicas, organosilanes, silsesquioxanes, and silicates. They can be used as additive agents or reactive monomers or comonomers.

Both silicones and silicas under fire conditions act in a condensed phase. They form an inorganic silica layer on a polymer surface, which blocks heat and mass transfer between polymer and flame front [9, 17].

Nanoparticles

One of the most promising and the most widely studied groups of FRs are those containing nanoparticles. Some call them even 'the future of fire safety' [64]. Due to their size, nanoparticles are very well dispersed in a polymer matrix and are efficient FRs even when added in small quantities.

They belong to one of three categories:
- **nanolayers**, which are called 2D nanoparticles. They have one dimension in nanometric size. They include nanoclays (layered silicates) [65, 66], graphite [59], layered double hydroxides (LDHs).
- **nanofibers**, which are named 1D nanoparticles. They have two dimensions in nanometric size. Cover carbon nanotubes, sepiolite.
- **nanoparticles,** which are named 0D nanoparticles. They have all three dimensions in nanometric size. Examples are polyhedral oligosilsesquioxane (POSS), spherical silica, metallic oxide particles (TiO_2, Fe_2O_3, Al_2O_3, ZrO_2, ZnO Bi_2O_3 [67], and several more), metallic hydroxide particles (alumina trihidrate $Al(OH)_3$ known also as ATH) and magnesium hydroxide $Mg(OH)_2$ (known also as MDH).

Nanoparticles are used as the only FR agent or else in numerous combinations with various other commercially used and newly discovered FRs.

Many commercially used mineral fillers have been prepared also in a nanosize and their fire performance studied. Among them are metal hydroxides, especially ATH [32, 43, 68, 69] and MDH [43, 70, 71] and also zinc borates [72].

Norouzi and coworkers [73] reviewed nanoparticle flame retardants for natural and synthetic textile polymers. Kandola and Deli [74] have done so for engineering applications. Christou, Stec and coworkers [75] discussed carbon nanotubes FRs and their health effects. Pereira and Martins [76] along with carbon nanotubes reviewed also nanoclays. Murariu et al. [77] gathered information on biodegradable nanocomposites containing flame retardants.

FIRE RETARDANCY OF WOOD – NATURAL POLYMER

We have noted above the ongoing process of replacing synthetic polymers with natural ones, wood in particular. Trees have been around for a long time – used by humans for a variety of purposes. The Great Basin Bristlecone Pines in northern California are the oldest living non-clonal organisms on the Earth - weather-beaten and resilient. The oldest tree, as yet unnamed, is believed to be about 5,100 years old now.

Wood consists of cellulose fibers in lignin [78]; see an artistic version of a cross-section by Raymond H. Pahler in Figure 10.
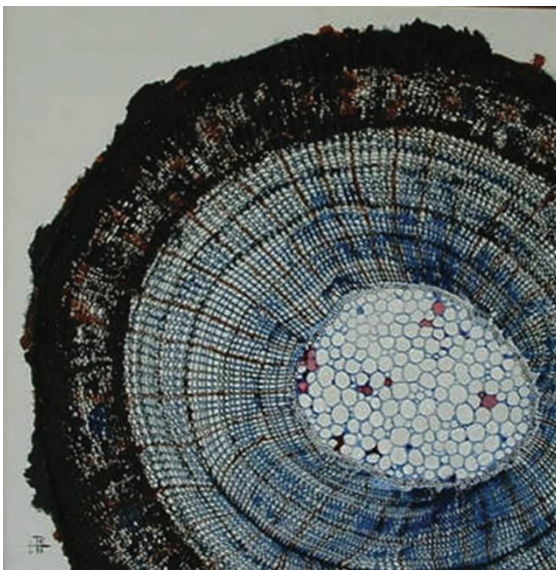

Figure 10. Cross-section of a tree as described in text.

Sweet and Winandy [79] studied fire behavior of boards made from southern pine – untreated as well as treated with a fire retardant (ammonium dihydrogen phosphate). Mechanical properties were determined after 1.0 and 1.5 years of exposure. Changes in the degree of polymerization and the chemical composition of α- cellulose isolated from the exposed wood were also measured. Four-point bending tests were made, providing the modulus of rupture (MOR) and the work-to-maximum-load (WML) values. The authors note that WML provides information on both strength and toughness. No evidence of hemicellulose or cellulose depolymerization was found. Instead, a strong relationship was found between the amount of mannan in the α-cellulose isolated from the wood and the MOR and WML values of solid wood.

Protection of wood from heat and fire hazards can be achieved by impregnation with boron-containing compounds. Kartal, Hwang, and Imamura [80] impregnated Sugi (*Cryptomeria japonica*) sapwood specimens with either boric acid (BA) or disodium octoborate tetrahydrate (DOT). The solutions were exposed to heat treatments at either 180 or 220°C for 2 or 4 hours. Chemical compositions and mechanical properties were determined for such specimens along with untreated and unheated specimens. The wood carbohydrates were significantly degraded in the heat-treated specimens. Apparently depolymerization and cleavage of acetic acid from the acetyl side chains took place. Increases in the amount of Klason lignin were found in heat-treated specimens – likely related to the ongoing removal of hemicelluloses during thermal degradation. Klason lignin procedure is a way to evaluate the amount of lignin present by hydrolysis involving H_2SO_4. A direct relationship was found between strength and hemicellulose losses of the specimens; as the hemicellulose content in the specimens decreased, losses in the MOR increased.

Let us note also a case when thermal degradation of polymers can be used to advantage. As described by Rebber, Willa and Koziej [81], such degradation of polymers with a well-defined

porous structure can provide microporous carbon materials usable for carbon dioxide absorption. As argued convincingly by the Hamburg authors, "Motivated by the air pollution that skyrocketed in numerous regions around the world" there is a great effort towards minimizing effects of this situation on human health by "discovering new classes of materials that separate, sense or convert CO_2".

Also, spent polymers subjected to high temperature in a controlled environment can be transformed into activated carbons. For example, waste ion-exchange resins were first carbonized at 600°C in inert atmosphere and then activated at 850°C by CO_2 [82]. Activated carbons with moderately developed porous textures (BET surface area of 178 m^2/g) were so created. Chemical activation by KOH used for preparation of activated carbons from waste polystyrene foam allows us to obtain sorbents with a very high BET surface area – up to 2700 m^2/g [83]. Activated carbons were obtained also from waste styrene–divinylbenzene copolymer [84] and from other thermoplastics, such as polyethylene (PE), polypropylene (PP) or polyvinyl chloride (PVC), but most of the studies focus on poly(ethylene terephthalate) (PET) [85].

CONCLUDING REMARKS

One has to take into account not only the behavior during the fire but also afterwards. Thomas Gernay [86] notes the 2004 collapse of an underground carpark in Switzerland. The cast-in-place concrete flat slab structure collapsed in punching shear *during the cooling phase* after a fire of limited severity. This is important for all involved - including members of fire brigades. The ISO 834 standard defines the fire resistance rating R as the time of the loss of structural stability under continuous heating. Gernay introduced a new parameter, Duration of Heating Phase (DHP) defined as the minimum duration of standardized natural fire that eventually leads to loss of stability. Stated differently, the column does not survive full burnout to the DHP fire. Both parameters are shown in Figure 11. We see that the column does not survive "a DHP fire" but it does survive a shorter natural fire – such as shown by the dashed line on the right hand side.
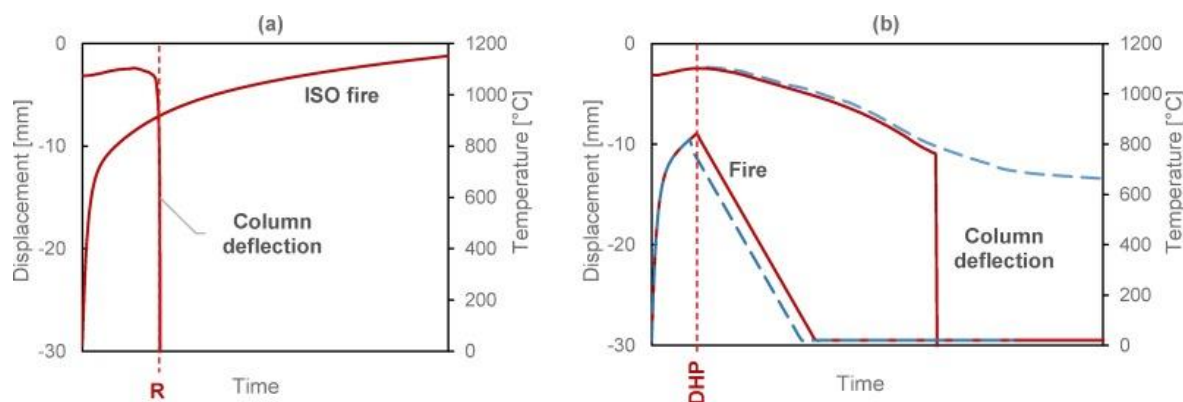

Figure 11. A column behavior during a fire.

Once FRs are applied at any location, the issue appears to be: "Do they remain in place ?"
Püttmann and coworkers [87] studied from this point of view organophosphate flame retardants (OPFRs) in indoor and outdoor air samples in the Rhine/Main area in Germany. The indoor samples were collected from private cars, private homes, floor/carpet stores, building material markets, schools, offices, and day care centers. Outdoor samples were simultaneously collected close to the indoor sampling locations. The total OPFR concentrations in indoor air ranged from 3.30 to 751.0 ng/m^3 with a median of 40.2 ng/m^3, approximately eight times higher than those in outdoor air (median 5.38 ng/m^3.) The median concentration of OPFRs in private cars was

180.3 ng/m^3, in private homes 12.5 ng/m^3, in schools 36.2 ng/m^3, in day care centers 31.8 ng/m^3, and in building material markets 31.2 ng/m^3.

Crewe, Stec and coworkers [88] conducted a fire experiment in a British 1950s style house. They measured temperature, smoke, CO, CO_2, and O_2 where in the lounge, stairwell, and front and back bedrooms. The front bedroom door was wedged open, while the door to the back bedroom was wedged closed. Contrary to optimistic expectations and with a relatively small fire load there was permeation of toxic fire gases throughout the property. Lethal concentrations of effluent were found at each sampling point. Poor state of repair and missing carpets in the upper storey contributed to a high degree of gas and smoke permeation. The available egress time was calculated as the time before the main escape route became impassable. Given known human responses to fire, such an incident might have caused fatalities to sleeping or otherwise immobile occupants.

Increasing the fire decomposition temperature was one of the objectives of Kharaev and coworkers [89]. They have synthesized bifunctional halogen-containing oligomers with various compositions and structures. They note that "Inserting halogen atoms into the structure of mocromolecular chain significantly increases the fire resistance of polymers".

Given the wide use range of epoxies, Brzozowski and coworkers [90] created a variety of epoxy compositions and determined their LOI values. Ordinary epoxies have LOI values around 21; epoxies containing diglycidyl ether of 1,1-dichloro-2,2bis(4- hydroxyphenyl)-ethylene bisphenol-C (BPC) have LOI = 34.6; BPC-containing epoxies with the Zn/Sn flame-retardant have LOI ≈ 44.

Zarzyka [91] obtained rigid polyurethane foams on the basis of hydroxypropyl derivatives of urea esterified with boric acid as polyol components and 4,4'-diphenylmethane diisocyanate. She reports that the flammability of foams is largely determined by the amount and concentration of carbamide groups.

We noted above the growing importance of natural wood. Also Gernay studied fire behavior of a timber column [92]. He concludes that collapse during the cooling phase is even more critical with timber than with concrete.

Fires can be studied also by computational simulation. Thus, Maragkos, Beji and Merci [93] used computational fluid dynamics with large eddy simulations of fire scenarios. This allowed turbulence, combustion and radiation modeling of a medium scale methanol pool fire.

There are fire safety regulations in virtually all countries. Buildings and roads are constructed following these regulations while – as noted at the beginning – the use of flammable polymers and PBMs in all kinds of applications is on the increase. Therefore, there is increasing demand for more and more fire resistant materials, which comply with the regulatory requirements and ensure safety for the users.

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