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Effects of ageing on the fire behavior of flame retarded polymers: A review

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Abstract

The influence of environmental ageing on the reaction-to-fire of flame retarded polymers is reviewed. Six types of stimuli have been identified as the most relevant parameters inducing fire behavior modification: temperature, moisture, UV radiation, ionizing radiation, chemical solvent and physical stress. This review provides a state of the art and current comprehension about the effects of ageing on flame retardancy of polymers. Various physical and chemical phenomena lead to ageing and deterioration (or sometimes improvement) of the flame retardancy of polymers: release of additives (not only flame retardants) through thermal migration, solubilization, abrasion..., chemical degradation of the flame retardant system, chemical or physical modification of the polymer structure (chain scissions, crosslinking, diffusion of water...). Obviously, ageing effects strongly depend on the material and the ageing scenario considered. Solutions to maintain flame retardant efficiency in aggressive conditions are also presented.

Keywords: Ageing, Flame retardant, Flame retardancy, polymer degradation

1. Introduction

Polymers are essential in many industrial sectors and applications because of their excellent properties. However, the susceptibility of these organic materials to fire is still a great concern. The use of flame retardants (FR) allows improving the fire behavior of polymers.

Global demand for flame retardants has increased over the last 30 years and it is forecast to rise by 5.4 percent annually to 2.6 million metric tons in 2016 [1]. This increase is related to the rise in the use of polymer-based materials and also to fire safety regulations which are more and more stringent [2].

Different ways have been suggested to improve the fire behavior of polymers such as the incorporation of flame retardants into polymers via melt blending (physical methods), the incorporation of flame retardants into the chemical structure of polymers (chemical method, i.e. via copolymerization or grafting) and the coating of a FR layer on the surface of the material. Different kinds of flame retardants are used in polymers such as mineral fillers, boron, phosphorus, halogen, nitrogen-based flame retardants. A flame retardant can act in vapor and/or condensed phases to limit the flammability of polymers [3].

The fire behavior is commonly defined by a set of parameters which are related to the reaction to fire of a material including ignitability, heat release rate, total heat release, flame spread, smoke production and toxicity [4]. The flame retardancy can be characterized using various tests such as cone calorimeter, Limiting Oxygen Index (LOI), UL-94, Single Burning Item (SBI), etc. [3,5].

Nowadays, the fire standard tests on polymer-based materials are currently carried out on newly manufactured samples. However, various ageing conditions can impair the flame retardancy throughout the lifetime. Therefore, it seems necessary to evaluate the influence of different kinds of ageing on the flammability of flame retarded polymers.

Textile industry is probably the first one which pointed out the durability of the flame retardancy as a major issue. Indeed, laundry treatments are regularly applied to textiles and flame retardant systems must resist to such treatments. A considerable literature has been devoted to the repeated washing of textiles. This specific issue is out of the scope of the present review.

In this article, we will address the influence of all other ageing scenario on flame retardancy of polymeric materials. This issue has attracted much less work, particularly considering the vast range of ageing scenario and materials. There are several ways to present these works. We have chosen to discuss the results according to the ageing scenario. The ageing sources are various: heat, moisture, ultraviolet or gamma irradiation, abrasion... and the combination of two or more sources. We particularly focus on the main points that emerge through the works already published. In the last section, we discuss briefly the different possibilities to improve the durability of flame retardancy.

2. Impact of ageing on flame retardancy

2.1. Preliminary remarks

Some issues are common to various ageing scenario. Many ageing conditions promote structural modifications of a polymer, like crosslinking and more generally

chain scissions. This last effect leads to a decrease of the molecular weight and then of the material viscosity. However, viscosity is an important parameter controlling the flammability. Indeed, in some fire tests, materials are rated according to their ability to drip. Dripping is obviously more severe for low viscous materials. As a surprising example, Nakashima et al. [6] have shown that highly flammable polyethylene does not burn in UL-94 vertical test when its molecular weight is 35000 g/mol or lower, due to severe dripping. Viscosity influences many other phenomena involved in flame retardancy: accumulation and migration of fillers at the surface [7], formation of a protective layer [8], intumescence [9], bubbling [10] ... Moreover, low molecular weight molecules are volatile and can decrease the thermal stability and promote early ignition. Nevertheless, this significant effect of ageing is scarcely taken into account in the study dealing with the influence of ageing on flame retardancy.

Ageing of materials in laboratory is most often tested on standardized polymeric specimen and not on “real” complex products. However, this discrepancy causes some problems. First polymeric material is sometimes only a part of the product and the other parts can influence the ageing of the polymer. For example, in cables, copper can catalyze the degradation. Migration of low molecular weight additives from inner part to sheathing in multilayer cables (containing insulation, bedding and sheathing parts) was already reported [11].

Migration extent depends on the surface/volume ratio of the product. The diffusion of water or oxygen into the material (which can promote various degradation reactions) is also strongly dependent on the geometry among other parameters [12]. Two cases can be defined: for thin specimen, the reaction (for example oxidation) rate is homogeneous within the thickness. For thick specimen, the kinetics is controlled by

the diffusion of the reactant. The critical thickness between both cases depends on various factors, including the exact conditions of the ageing scenario. However, the geometry of standardized samples studied in laboratory is not necessarily close to the geometry of real products.

Accelerated ageing tests (in more severe conditions) are quite often used to simulate a long natural ageing. As explained above, the extent of diffusion-controlled phenomena depends on ageing conditions. For example, the thickness of the oxidized layer (TOL) of low-density polyethylene (LDPE) after radiochemical ageing increases with low dose rate. In thermal ageing, the TOL is a decreasing function of the temperature [12]. Moreover, accelerated ageing tests cannot generally accelerate several independent phenomena in the same extent. However, ageing of complex materials can induce various modifications. Therefore, such tests should fail to predict the exact influence of natural ageing on the structure and the composition of a material.

The last remarks do not mean that studies of simple standardized specimen in accelerated ageing conditions are worthless. Such studies are still needed to separate and assess every phenomena occurring during ageing. But it is necessary to keep in mind that natural ageing of “real” products is not perfectly simulated.

2.2. Thermal ageing

The first effect induced by the thermal ageing is the migration (followed by exudation) of low molecular weight flame retardant additives.

Inata et al. [13] studied the influence of thermal ageing (at 110, 130 and 145 °C) on the migration of 16 halogenated compounds incorporated into polypropylene (PP).

The weight loss of PP during ageing is assigned to the exudation of flame retardants and follows an exponential function (see Figure 1). The migration is not only dependent on the temperature and the molecular weight of the flame retardant but also on its structure. Migration is higher for aliphatic brominated additives, followed by molecules containing only one aromatic rings. Molecules containing double aromatic rings, phosphate or isocyanuric groups hardly migrate, except when aromatic rings are directly connected. Flame retardants exhibiting melting point higher than processing temperature are dispersed as large particles. Nevertheless, quite unexpectedly, migration is also observed for these additives.

In these experiments, thermal ageing was carried out at high temperatures. Nevertheless, the authors have calculated activation energy of migration to estimate the migration rate at lower temperatures (corresponding to service life). In some cases, migration can be significant. For 2,4,6-Tribromophenyl-2',3'-dibromopropylether (TBP-DP) which exhibits the highest migration rate, the half-value period (corresponding to the loss of 50% of additive) at 30 °C is only 5000 hours, i.e. 200 days.

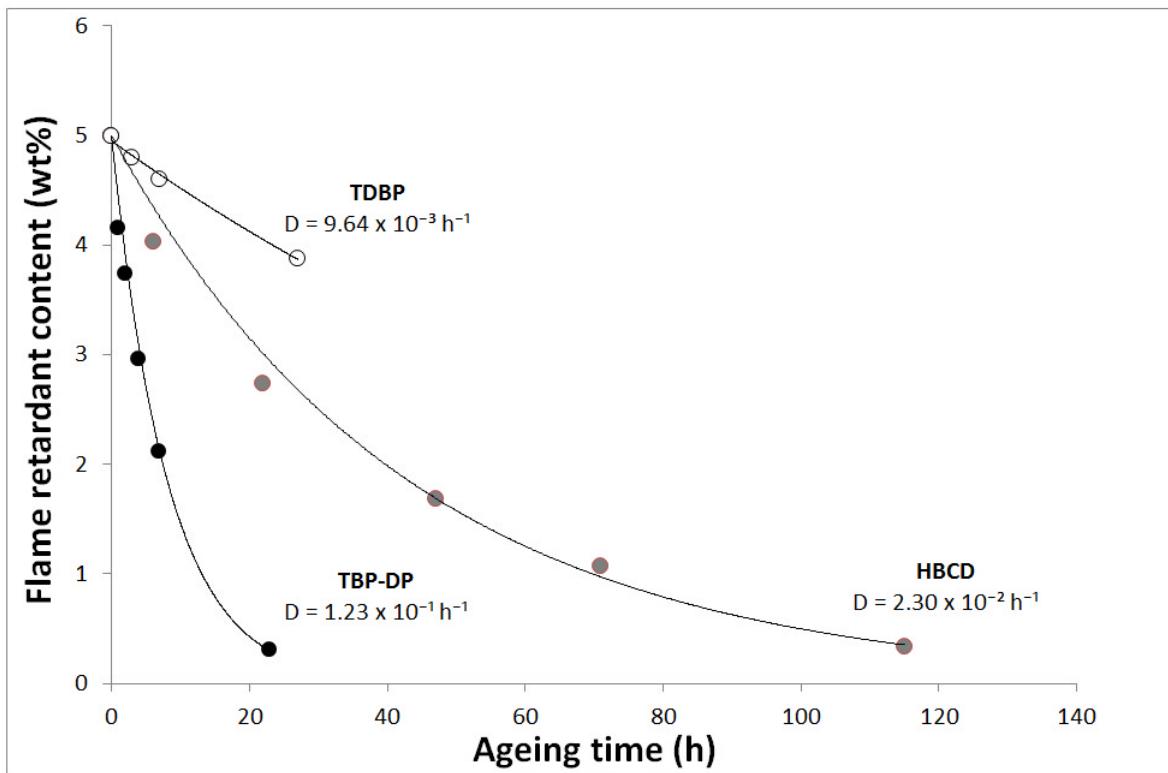


Figure 1 – Flame retardant content in PP versus ageing time at 145 °C for various flame retardants (TBD-DP: 2,4,6-Tribromophenyl-2',3'-dibromopropylether, HBCD: 1,2,5,6,9,10-Hexabromocyclododecane, TDBP: Tris(2,3-dibromopropyl)phosphate) – D is the diffusion coefficient calculated by the authors (Graph drawn from the data in [13])

The authors have also measured limiting oxygen index (LOI) after ageing for some flame retardants. Figure 2 shows the limiting oxygen index of PP initially filled with 5% of TBP-DP. During ageing, the flame retardant content decreases due to exudation and LOI decreases. The relation between LOI and flame retardant content is roughly linear.

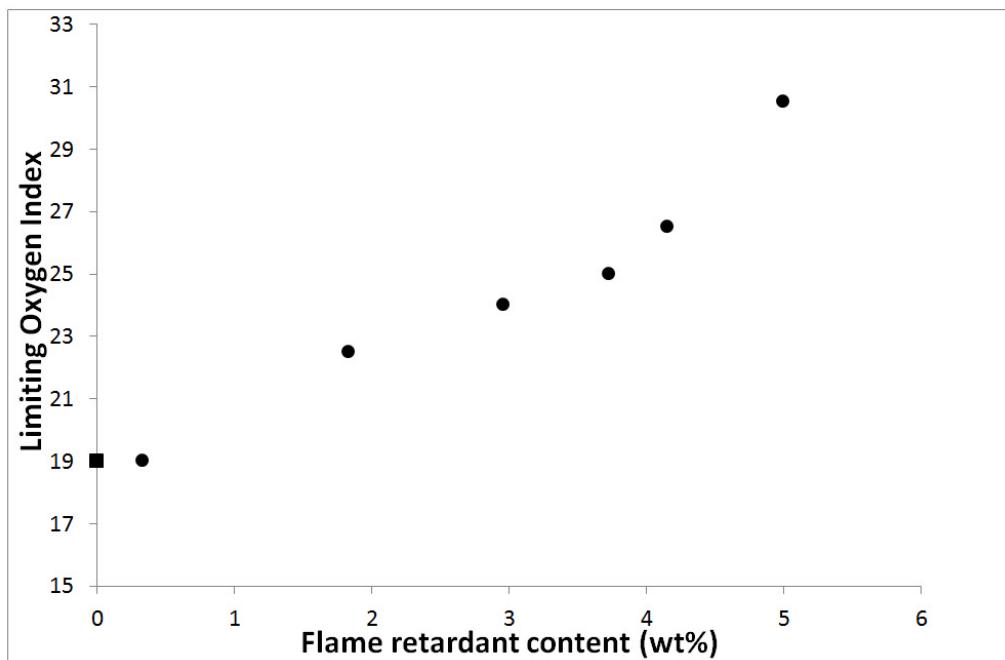


Figure 2 – Limiting oxygen index of PP flame retarded with TBP-DP according to the flame retardant content (decreasing with ageing time at 145 °C) – Black square corresponds to the value for pure PP (graph drawn from data in [13])

Migration under the effect of temperature may also concern nanoparticles. This phenomenon has been invoked to explain the particular ability of nanoparticles to generate a protecting layer during combustion. In most cases, migration has been studied in a fire situation but not during service life (at moderate temperature). But some results could be extrapolated in some extent. As an example, Lewin et al. [14] have comprehensively studied the migration processes of organomodified nanoclays into polypropylene during annealing at intermediate temperatures (200-300 °C i.e. much lower than ignition temperature). After 2 hours at 200 °C the clay ratio between the upper and the lower surfaces of the sample reaches 2.86 showing strong enrichment of the upper surface. The authors have identified several phenomena: aggregation of nanoparticles, exfoliation and migration. The former is only dependent on the surfactant decomposition and then should not occur at moderate temperatures

(at least in their study). The two last ones are also partially dependent on the surfactant decomposition and therefore it appears rather difficult to assess at which extent they can occur during ageing at service conditions. Recently Colonna et al. [15] studied the effect of thermal ageing on the combustion behavior of a EVA-organically modified clay nanocomposite. Contrarily to previous studies, ageing was carried out close to but below the melting point of the polymer matrix (90 °C). It was highlighted that upon ageing nanoparticles dispersion changed from an intercalated to an exfoliated structure. As a consequence, the fire behavior was significantly modified after thermal ageing. It was observed that nanoclays move rapidly to the surface promoting the formation of a layer likely to trap fuel and thus delaying ignition. On the contrary, pHRR was increased significantly from 430 to 657 kW m⁻².

All additives (and not only flame retardants) can undergo migration and exudation during thermal ageing. In some cases, additives can be present in high amount and their contribution to flammability can be significant, particularly for low thermal stability organic compounds. For example, PVC-based plastisols contain 60 phr of plasticizers for 100 phr of PVC. According to the nature of plasticizers, mass loss of plastisols due to additives migration can reach more than 1% at moderate temperature (50 °C) after only 420 min in air [16]. While PVC is a low-flammable polymer, organic plasticizers in such amount impact significantly the flammability of plastisols. Therefore, additives release can reduce the flammability but their migration and accumulation close to the surface can also be detrimental. Generally, exudation is not only dependent on heat-controlled diffusion but also on evaporative conditions.

Emanuelsson et al. [11] investigated two commercially available cables in terms of flammability (measured using a cone calorimeter) after accelerated thermooxidative

ageing at 80 °C in an oven for 1, 3, 8 and 16.5 weeks. The first cable is based on an ethylene butylene acrylate (EBA) copolymerized with ethylene with CaCO₃ and silicon gum. The second cable consisted of PVC, chalk and phthalate plasticizers. The flame retardancy of the polyolefin cable does not change appreciably after ageing. On the contrary, some changes occur on the heat release rate curve for the PVC cables (it must be pointed out that these changes are modest). In particular, the first peak of heat release rate (assigned to the degradation of the sheathing) slightly increases after one week of ageing while the second peak (assigned to the degradation of the inner parts) decreases. Moreover, the time-to-ignition also tends to decrease (from 25 to 17 s with an irradiance of 50 kW m⁻²). From various analyses, the authors excluded the dehydrochlorination to explain these results. They observed a slight migration of plasticizers from the inner parts to the sheathing. The concentration of plasticizers in the whole cable decreases during ageing from 26.1 to 25.6% (due to migration and release, as discussed above) but this concentration increases from 20.1 to 21.1% into the sheath. The authors assumed that this migration of plasticizers explains at least partially the change of the HRR curve shape and the decrease of the time-to-ignition.

Thermal ageing of a chlorosulfonated polyethylene (CSPE) containing antimony trioxide was studied by Clough [17,18]. Loss of chlorine and antimony (discussed just below) is observed but during a first period, the chlorine and antimony contents increase. The author explained this result by the loss of other volatile components present in the material. Moreover, LOI significantly increases during ageing, from 39 for unaged material to 43 and 50 after 4 and 8 months at 110 °C. This unexpected result was assigned to the loss of relatively volatile and non chlorinated low molecular

weight additives as evidenced by the decrease of the weight loss in thermogravimetric analysis (TGA) at low temperature (< 425 °C) for aged samples (from 25% for unaged cable to 15.1% after 8 months of ageing). It means that these additives degrade significantly the flame retardancy.

Not only migration-induced release but also degradation can be expected during thermal ageing. Clough [17,18] has also studied the thermal ageing of various flame retarded ethylene-propylene rubbers used for nuclear plants applications. The materials studied are halogenated and also contain antimony trioxide as synergist. The release of chlorine and antimony during ageing is strongly dependent on the materials. For most of EPR flame retarded with halogenated compounds, no appreciable release was observed. But for one of them (called EPR V), EPR flame retarded with partially chlorinated paraffin and antimony trioxide, the release is significant because the chlorinated paraffin can easily undergo an intramolecular dehydrochlorination. Antimony trioxide is non-volatile and the release of antimony is preceded by a chemical reaction (HCl reacts with antimony trioxide to give volatile $SbCl_3$). Activation energy for antimony loss was calculated and the time for loss of 25% of antimony content was measured or calculated for various temperatures (Figure 3). Obviously the loss increases with the ageing temperature. But it may be pointed out that antimony release is very low in real (i.e. moderate) service temperature. For example, 600 years are needed for a loss of 25% of antimony content at 50 °C.

Nevertheless, LOI of EPR V aged at various temperatures and times does hardly change. For example LOI decreases slightly from 28 to 26.5% after ageing at 110 °C

during 8 months. According to the Figure 3, such ageing corresponds to a loss of antimony much higher than 25%.

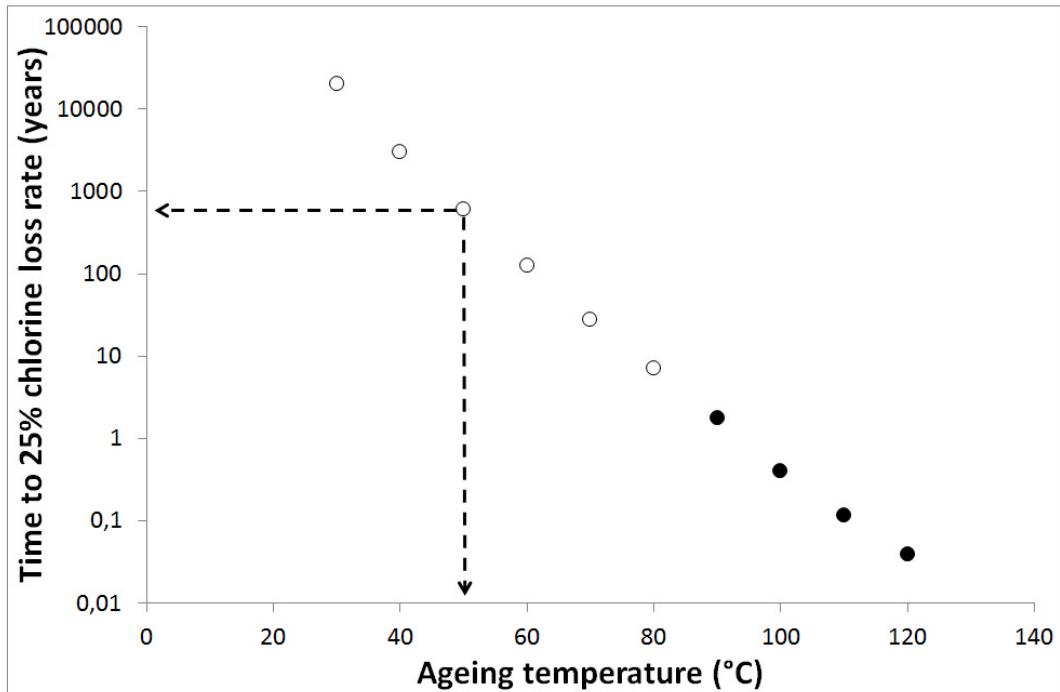


Figure 3 – Time for loss of 25% of initial antimony content in flame retarded EPR at various ageing temperatures (black circles correspond to experimental measurements, white circles correspond to calculated values using Arrhenius plots (graph drawn from data in [17]))

Dechlorination due to thermal ageing concerns not only flame retardants but also poly(vinyl chloride). Dembsey and Williamson [19] have studied PVC foam wall covering using a large fire test (according to Uniform Building Code Standard N° 42-2). The authors noted that preheating of materials leads to higher flammability because hydrogen chloride is released from PVC. Then less chlorine (well-known as flame poisoning) is available during burning. Nevertheless, in this study, preheating temperature is in the range of 230 to 280 °C. At moderate temperatures, dechlorination is probably much weaker or negligible.

We have previously noted that thermal ageing can improve the flame retardancy (see above the results obtained by Clough on flame retarded chlorosulfonated polyethylene). Other studies confirm that thermal or thermo-oxidative ageing can lead to such improvement of the flame retardancy. Zuo et al. [20] studied with the effect of thermal-oxidative ageing on flammability of long glass-fiber reinforced polyamide 6 (PA6/LGF) composite containing tris(tribromophenyl) cyanurate and antimony trioxide. The samples were aged for 10, 30 and 50 days in thermal-oxidative condition at 160 °C. UL-94 rating remains V-0 even after 50 days of ageing. A positive effect of ageing is observed for LOI test (from 25.6 to 37.4 after 50 days of ageing). In cone calorimeter (irradiance 50 kW m⁻²), peak of heat release rate (pHRR) decreased from 108 to 72.1 kW m⁻² (see Figure 4). The authors explain the enrichment of the surface in flame retardants (assigned by the authors to migration) allows FR acting sooner leading to the reduction of the pHRR (which occurs few seconds after ignition). Moreover, ageing may promote charring (the residue content in cone is enhanced from 31.5 to 35% after 50 days of ageing). On the contrary, the authors claimed that ageing does not modify the mode-of-action in gas phase (even if the effective heat of combustion appears to slightly decrease for a 50 days-ageing). Unexpectedly time to ignition (TTI) in cone calorimeter is stable (55-57 s) up to 30 days-ageing but increases very significantly up to 145 s after 50 days-ageing. No reasonable explanation was provided by the authors.

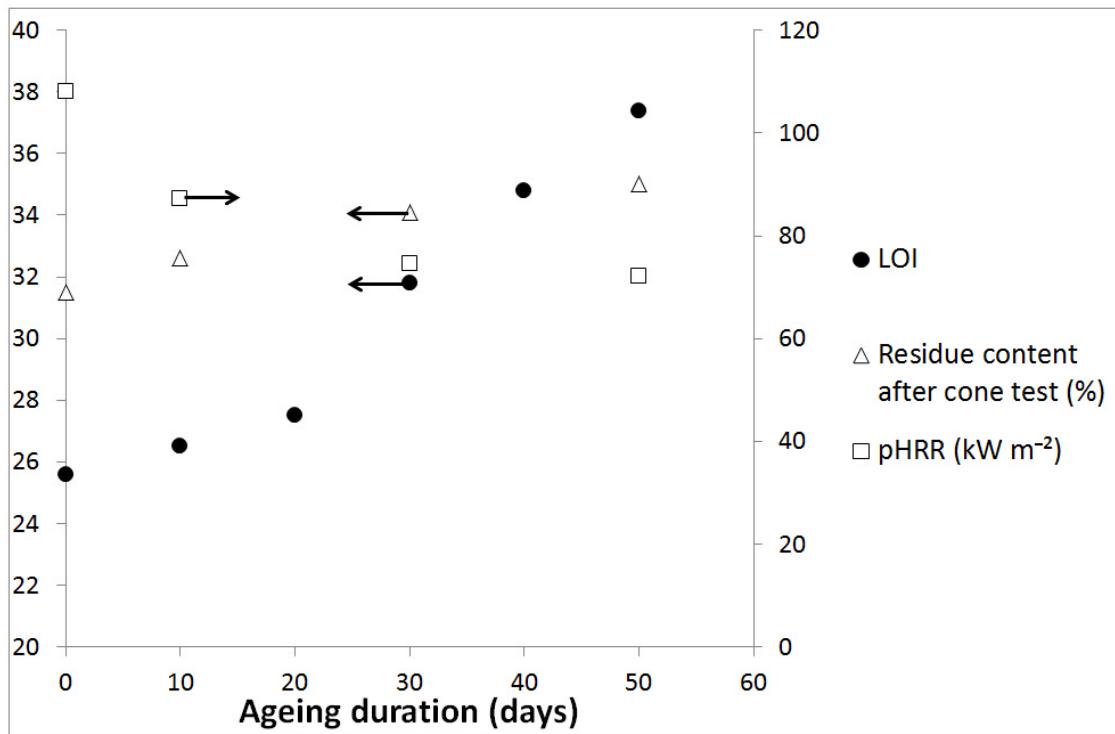


Figure 4 – Change of LOI, pHRR and residue content in cone calorimeter with ageing duration in air at 160 °C (graph drawn from data in [20])

Some specific cases concern ageing at very high temperatures. It is particularly the case of low-emissivity materials used in aeronautics field. Therefore some studies have been carried out about the influence of thermal ageing or thermal shocking on emissivity. However emissivity is also an important parameter controlling the heat transfer into a material and thus its flammability. Ignition in cone calorimeter (radiative heat flux) is dependent on emissivity among other parameters [21] and Schartel et al. [22] have recently showed a nice flame retardancy strategy by coating a material with low emissivity layer. This strategy delays greatly the ignition. However, it must be noted that such strategy is only available in case of radiative heat flux. Moreover other flammability properties (peak of heat release rate, total heat release, etc...) are not modified.

Hu et al. [23] have studied the thermal ageing of different low-emissivity materials. In a first article, a polysiloxane coating containing aluminum particles was heated up to 600-700 °C and maintained at this temperature during 100 h. At 600 °C, the material is inert and its emissivity is not modified. At 650 °C, emissivity increases slightly (from 0.2 to 0.3) due to cracks and gaps which make the surface rougher. At 700 °C, the emissivity increases quickly to 0.9 (after only 20 h of ageing). Increase of the surface roughness and mainly oxidation of aluminum particles explain these results.

In another article, the same authors compare the influence of two modes of ageing on emissivity of an epoxy-siloxane coating containing 40 wt% of aluminum particles [24]. The first mode is thermal ageing and consists in maintaining the material during 50 h at a given temperature in air. The second mode (called thermal shocking) consists in 20 cycles of heating/cooling. During a cycle, the material is maintained at a given temperature during 10 minutes followed by a water quenching. Exfoliation of the coating from the substrate is found as the main mechanism of degradation which leads to a sudden increase of emissivity for a critical temperature. Thermal shocking is more detrimental than thermal ageing (see Figure 5).

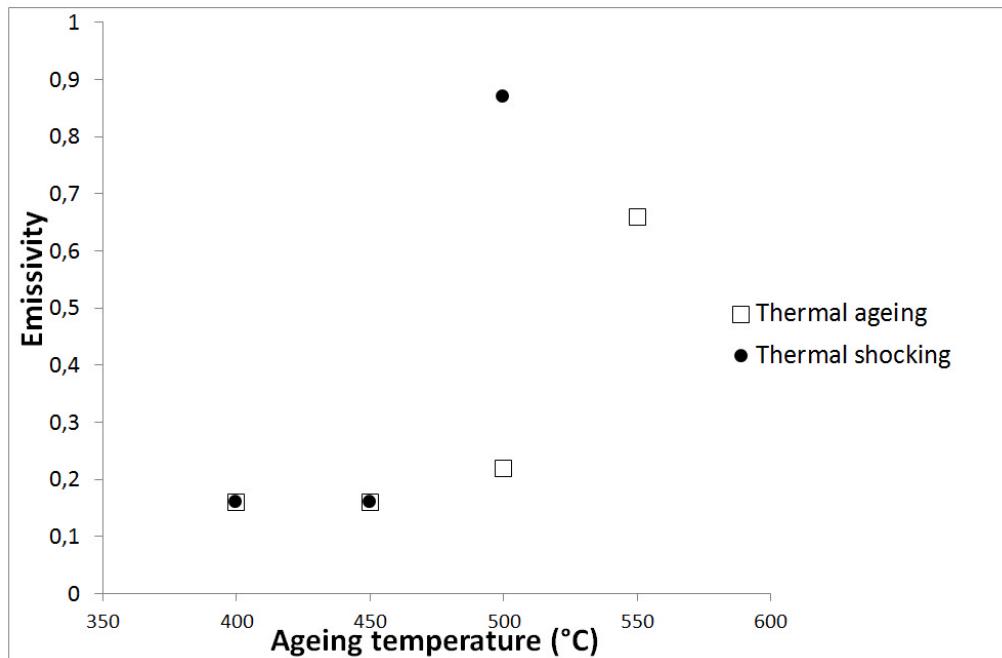


Figure 5 – Emissivity of epoxy-siloxane coating containing aluminum particles versus ageing temperature or two modes of ageing (graph drawn from data in [24])

Even at room temperature, some materials can evolve. Eaves and Keen [25] have studied commercial polyurethane foams. More specifically they measured the lower internal temperature allowing the beginning of an exothermic reaction. This reaction is self-sustaining and spreads from the center to the surface of the foam. Finally the foam burns when the reaction reaches the surface. The critical temperature is found increasing with ageing in ambient temperatures and humidity (Figure 6). To explain the greater stability of aged foams, the authors assumed that residual reactive species from foam manufacture disappear during ageing. Another hypothesis is that the surface oxidizes and becomes more resistant to further reaction.

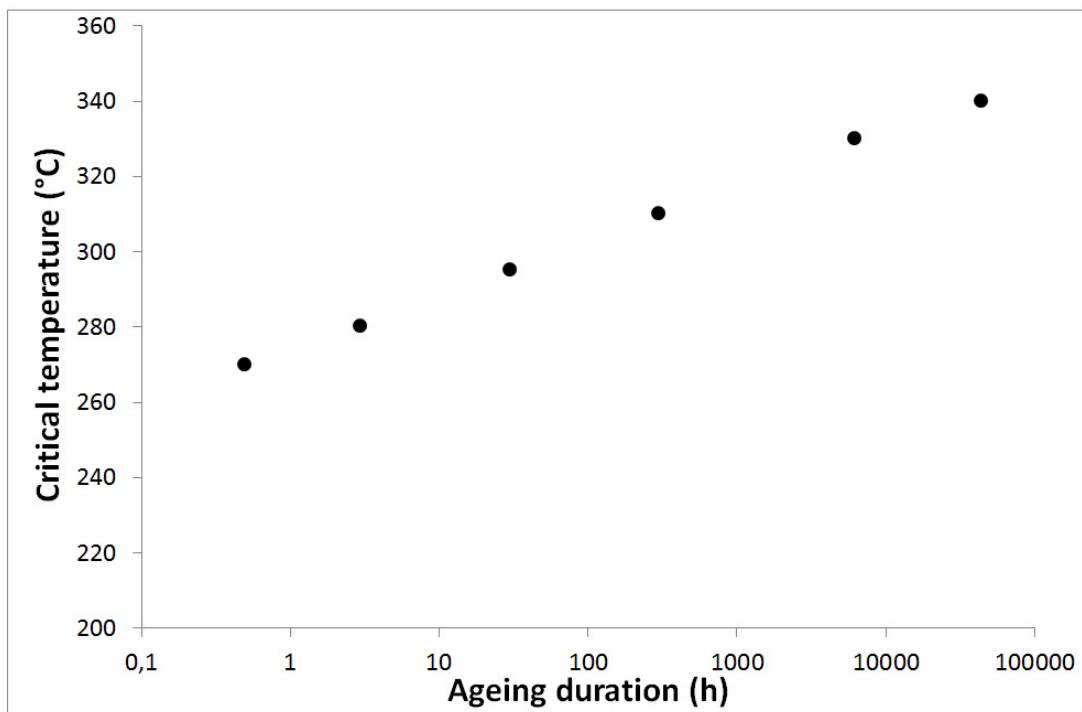


Figure 6 – Critical internal temperature to induce exothermic reaction into polyurethane foam versus the ageing duration of the foam in room temperature and humidity (graph drawn from data in [25])

All the previous articles showed significant changes after thermal ageing about flame retardancy, degradation or migration of additives. Nevertheless, it must be pointed out that other studies have evidenced a good stability of some systems against thermal ageing. For example, Simonson et al. [26] have studied high impact polystyrene (hiPS) filled with 11% of decabromodiphenylether before and after ageing at 80 °C in air during 1200 h. Considering that an increase of 10 °C corresponds to double the ageing duration, the authors calculated that these conditions represent 8 years at room temperature. Neither degradation nor migration of the flame retardant was observed and the material maintains its UL-94 V0 rating.

2.3. Ageing in presence of water/moisture

In the case of hydrolysable polymers, the presence of moisture can lead to dramatic changes in molecular weight and viscosity, which is an important parameter controlling the flame retardancy as previously explained.

Flame retardant system can be also much degraded in presence of water. In a recent work, Jimenez et al. [27] investigated the influence of different ageing scenario on the fire protective behavior of an epoxy-based intumescent coating used to protect a steel structure. This 1.5 mm-thick coating system was based on an epoxy resin containing ammonium polyphosphate (APP), melamine (MEL), and titanium dioxide (TiO_2). Different conditions of ageing were performed: humid (80% moisture) and hot ($70\text{ }^{\circ}\text{C}$) atmosphere for 2 months, immersion for 1 month in distilled or salt water at $20\text{ }^{\circ}\text{C}$. The samples were submitted to a burner (35 kW m^{-2}) in a furnace test and the backside temperature of the samples was measured using an infrared pyrometer. The authors considered the time taken to reach $400\text{ }^{\circ}\text{C}$ as the time of failure. The fire protective effect of coating is slightly deteriorated after ageing in distilled water (expansion ratio is reduced from 8 to 6) and considerably decreased after ageing with salt water. The time of failure is 285 s, against 700 s for the reference coated steel and the intumescent phenomenon disappeared, after ageing in salt water.

Different analyses were performed in order to explain the chemical changes occurring in the coating. A preliminary observation shows that adhesion between coating and steel remains correct after immersion in distilled and salt water. The results showed that distilled water leads only to the formation of polyphosphoric acid (from APP) which can be easily dissolved and removed from the matrix. This loss of

APP is only observed in the extreme surface of the coating and therefore the degradation of the intumescence is limited. Melamine is not modified.

On the contrary, salt water induces many phenomena. Sodium and chlorine migrate deeply in the coating. Ammonium polyphosphates are transformed into more soluble sodium polyphosphates (solubility in water 14 wt% against 0.5 wt% for APP). These species can be easily removed from the coating. NH_4^+ ions combine with Cl^- are also released from the coating. Melamine is also dissolved and released into water. This dissolution is promoted by chloride ions. Coating is found full of pores. Both char promotion (due to phosphates) and expansion (due to ammonia and melamine) are prevented. Moreover, the authors note that sodium polyphosphate is more thermally stable than APP. Therefore its decomposition during burning occurs too late to promote charring.

Wang et al. [28] have studied the influence of ageing on the intumescent structure itself. The coating protecting a steel plate is not fully described but is also based on APP, melamine and pentaerythritol. One cycle of ageing corresponded to 8 h at 40 °C and 98% of relative humidity followed by 16 h at 23 °C and 75% of relative humidity. After several cycles, the expansion ratio of the intumescent structure (and then the porosity) decreases and the bubble size increases (see Figure 7). Both phenomena lead to an increase of the thermal conductivity of the expanded char. The steel plate is less insulated from heat and its temperature increases faster.

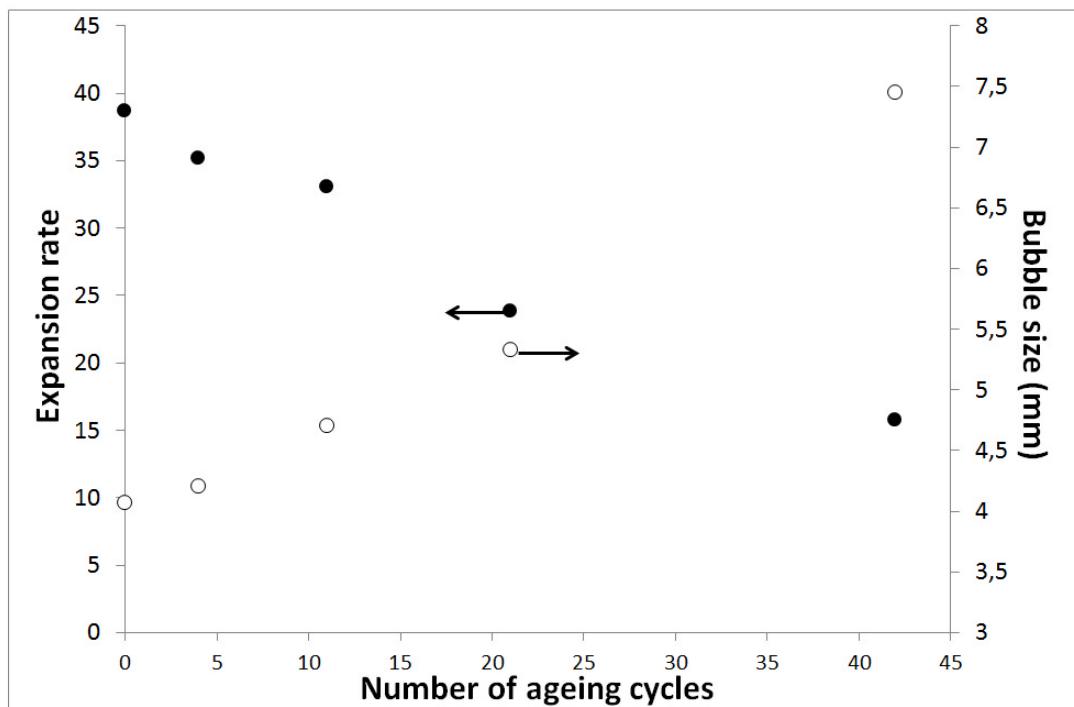


Figure 7 – Change in structural properties of the char layer of a commercial intumescent system after ageing (graph drawn from data in [28])

Water can be detrimental by modifying chemically the materials (polymer and/or flame retardant) but its presence can also affect the flame retardancy even without any chemical modifications. Oztekin et al. [29] have recently highlighted the great and rather unexpected influence of moisture on the flame retardancy of Polyether ether ketone (PEEK) studied in cone calorimeter. When a low amount of moisture is present into PEEK (the “wet” PEEK contains 0.73 wt% more than the “dry” PEEK), the water is released just after the polymer melting (at 343 °C). This release leads to vigorous bubbling and changes the thermo-optical properties of the material. It results in shorter time-to-ignition (from 207 to 110 s at an irradiance of 50 kW m⁻²) but lower peak of heat release rate (from 355 to 280 kW m⁻²). Such influence of the moisture was further studied for other polymers [30].

Another case of the dramatic influence of moisture “trapped” into a polymer was presented by Lay and Gutierrez [31]. These authors studied the fire behavior of both phenolic and polyester laminate composites after an accelerated ageing in salt water. 6 layers of glass woven roving were used for the reinforcement. The ageing was carried out by immersion of samples in synthetic salt water solution at 60 °C for 1000, 2000, 4000 and 8000 hours. Cone calorimeter test was carried out at 50 kW m⁻² of irradiance. The results of cone calorimeter showed that initially (before ageing) the phenolic composite presented a better fire behavior compared to the polyester composite (peaks of HRR were 100 and 300 kW m⁻², respectively and time to ignition was 6 times longer for phenolic resin). The peak of HRR remained approximately the same after ageing for the polyester composite. In the case of the phenolic composite, after ageing (1000-hours immersion) the sample exploded during cone calorimeter test. This phenomenon was assigned to microvoids formed by the water evolved during curing. These microvoids allow a high water uptake (7-8 wt% but maybe it is not the whole water content) occurring during the first 500 hours of ageing. The water trapped in the microvoids was suddenly vaporized during the burning leading to the violent explosion of the matrix.

In another study, Feih et al. [32] confirmed that phenolic composites do not provide good structural performances in case of fire, despite their very low flammability. In this case, water is initially present as solvent and is also a by-product of the condensation curing at a higher content than in the Lay and Gutierrez study (20-25 wt%). The authors recommend natural or artificial ageing (not in water obviously, but in air at 80 °C during 250 h) to decrease the water content to 10 wt%. In this case, delamination and matrix cracking due to water vaporization are strongly reduced and

the structural performances (i.e. the resistance to failure under static loading during fire) are significantly enhanced.

Lay and Gutierrez [33] studied the modification of the fire behavior after ageing of flame retarded thermoset composites prepared by DCN (“Direction des Constructions Navales, France”). These composites are used as external structure of warships and therefore the effect of ageing, in presence of salt water, on fire behavior is very important. These composites were based on a diglycidyl ether of bisphenol A (DGEBA)-type vinylester resin (VE) containing 10 layers of glass woven roving. Four types of samples were tested: VE composite without FR (VE std), brominated VE composite (VE br - bromine is brought by brominated DGEBA), VE br with antimony trioxide Sb_2O_3 (VE Sb_2O_3) and VE br with zinc hydroxystanate $ZnSn(OH)_6$ (VE ZHS). The ageing process was carried out in a salt water solution at 70 °C for 500, 1000 and 2000 h and cone calorimeter test was performed at 50 kW m⁻² of irradiance.

The results in cone calorimeter tests showed all possible trends. Time-to-ignition does not change after ageing for non-flame retarded composite, but increases for other composites (the extent of the increase is variable). pHRR is also unchanged for VE std and VE ZHS but increases for VE Sb_2O_3 . On the contrary, pHRR decreases for VE br. Finally specific extinction area (SEA) is unchanged for VE std but increases for the flame retarded composites after 500h of ageing. But for longer ageing duration, SEA decreases. These results are quite surprising while the main component of the flame retardant system (brominated DGEBA) is the same and only the synergist changes (no synergist or 5% of Sb_2O_3 or ZHS). Unfortunately authors did not attempt to explain these results.

2.4. UV-irradiation / Weathering

We have seen that thermal ageing may promote migration and exudation of flame retardants. But while temperature in service is generally much lower than processing temperature (which sets the minimal temperature of stability of flame retardant), it is doubtful that thermal ageing can degrade the flame retardant structure. On the contrary UV-rays can induce such modifications. Ghanem and Delmani [34] have studied the migration of decabromodiphenyl ether (decaBDE) used in backcoated textile samples. After ageing during 200 days at various temperatures, the authors extracted decaBDE in acetonitrile using Soxhlet apparatus. Loss of decaBDE increases with the temperature and reaches 39.4 wt% after ageing at 90 °C. The rate constants of decaBDE release were estimated at 0.36×10^{-2} , 1.03×10^{-2} and 3.6×10^{-2} per day respectively after ageing at 25, 60 and 90 °C. After UV-irradiation during 130 h (UVA-340 lamp, irradiation intensity of 1.25 W.m^{-2}), the loss of decaBDE reached to 28.5 wt%. The constant rate was higher than for ageing at 90 °C: 3.94×10^{-2} per day. Moreover, in this case, not only migration but also degradation of decaBDE into lower congeners (nonabromodiphenyl ethers) was observed. Photodegradation led to photodebromination.

Kajiwara et al. [35] have also observed the photodegradation of decaBDE into less-brominated congeners. They also observed the formation of poly(brominated dibenzofurans). The degradation of decaBDE is related to its chemicals structure and particularly to the ether bond. Indeed, decabromodiphenylethane does not degrade significantly in the same conditions. Moreover, the photodegradation was enhanced when hiPS/decaBDE samples were hydrated. The decrease of decaBDE content is very fast but the authors noted that this kinetics is dependent on the preparation of

the material (pulverized plastics in this study). Finally, the degradation is much slower in a TV casing samples, probably due to the presence of additives absorbing photoenergy.

In the introductory part, we have pointed out that viscosity is an important parameter controlling the flammability. Therefore, flame retardancy can significantly decrease after photo-ageing due to the detrimental effect of the flame retardant on the photo-stability of the polymer.

It is now well-known that flame retardants (and particularly halogenated ones) can promote the fast ageing of polymers. Sinturel et al. [36] have devoted several papers to study the photo-oxidation of polypropylene in presence of flame retardants. Oxidation rate is increased in presence of decaBDE and induction period is dramatically decreased. Such effects are observed from 5% of flame retardant and do not increase very much for higher contents. On another hand, flame retardants allow protecting the core of sample due to an inner filter effect in the UV range (i.e. flame retardants decrease the thickness of the photo-oxidized layer). When exposed to UV-rays, decaBDE degrades through the homolytic cleavage of the C-Br bond [37]. The formation of a reactive bromine radical leads to the hydrogen abstraction on the polymer backbone.

Torikai et al. [38, 39] evidences that various brominated flame retardants accelerate the photodegradation of polystyrene and polypyropylene. Photodebromination of decaBDE leads to HBr release which may promote photolytic decomposition of the polymer matrix [40]. Moreover, Sinturel et al. [41] have shown that the amine groups of a hindered amine stabilizer (HAS) react with hydrobromic acid (released by the photolysis of decaBDE) to form amine salts at the surface of the sample. HAS

migrates from the core to the surface and a depletion zone was observed by the authors at intermediate depth. Due to the formation of inactive amine salts, photo-oxidation of polypropylene is significantly enhanced.

Other types of flame retardant do not show the same trends. Chantegraille et al. [42] have studied a PP flame retarded with an intumescence system based on ammonium polyphosphate and a synergist containing nitrogen. The authors observed that the flame retardant can be photo-oxidized but not degraded by photolysis in the absence of oxygen. Moreover, even if its oxidation starts much earlier than the oxidation of polypropylene, both oxidations occur independently and no influence of the flame retardant on the photo-oxidation of PP was detected.

The effect of 5 or 10 wt% of layered double hydroxide (LDH) and organomodified montmorillonite (OMMT) on polypropylene photo-oxidation was also studied [43]. Polypropylene grafted with maleic anhydride was used as compatibilizer. As a result, a good dispersion of nanoparticles was achieved. Polypropylene photo-oxidation is significantly enhanced by OMMT. The influence of LDH depends on divalent cations. Mg^{2+} has a degrading effect while Zn^{2+} does not accelerate the oxidation of the polymer.

Many other examples can be found in the comprehensive review of Wilén and Pfaendner [44] devoted to the possible mutual interactions between FR and stabilizers. Mineral fillers can adsorb stabilizers onto their surface, reducing their efficiency. Polyphosphoric acid (released from the decomposition of phosphorus-based flame retardant, like ammonium polyphosphate) interferes with HALS. Fortunately, other systems (melamine phosphate) do not exhibit any antagonism effect with stabilizers [45]. If the authors conclude that “phosphorus and nitrogen-

based FRs influence the (photo) oxidative stability of polymers less than brominated compounds and they show no or less antagonism with HALSs", they also claim that the impact of halogen-free flame retardants "has been studied to a lesser extent and is less known".

On the other hand, it is questionable that low penetrating UV-rays can effectively degrade the flame retardancy, while only the exposed surface of the polymer can be modified. Hence, Rosik et al. [46] have identified several degradation mechanisms for hiPS containing decaBDE or HBCD with antimony trioxide as synergist after photooxidation or weathering: photochemical decomposition of decaBDE, oxidation of the polymer, cracking and erosion of the polymeric surface (during weathering only). The decomposition of decaBDE leads to a decrease of its content in the thin surface layer (about 10 µm). Nevertheless, after longer duration of weathering, the decaBDE content increases in the surface layer due to significant erosion of the polymer. Even if all these phenomena modify some properties (impact strength and colour), flammability is not changed. UL-94 rating is maintained to V0 or V2 (according to the material) and LOI is stable, even after 1450 h of photo-oxidation or 185 days of weathering. The authors concluded that the service life of such materials is not limited by the decrease of flame retardant properties but by other properties which are significantly modified sooner.

However flame retardancy can be ensured by a surface protective layer (coating). In some other cases, even if flame retardant is dispersed in the bulk, its efficiency may depend on the fast formation of a barrier layer and then involves mainly a rather thin layer of the material exposed to heat. Similarly, flammability of a polymer may be

mainly driven by the properties of a thin surface layer. In all these cases, photo-ageing may be influent on flame retardancy.

Hence, Diagne et al. [47, 48] observed that polypropylene grafted with maleic anhydride (PP-g-MAH) exhibits better flame retardancy (measured in cone calorimeter) after UV irradiation or weathering. Both ageing scenario may promote the crosslinking of PP-g-MAH in a thin surface layer (oxidation profile shows that UV-rays modify only a 150 µm-thick layer). According to the authors, the improved fire performances after ageing are related to this crosslinking. On the contrary, when nanoclays are incorporated into PP-g-MAH, flame retardancy is deteriorated after ageing. The authors explain that nanoclays can reduce the formation of radical by attenuating the UV-rays penetration and by preventing the radical mobility. Therefore, crosslinking is inhibited. Nevertheless, it must be pointed out that the cone calorimeter results are unclear due to the large uncertainties on the data. Moreover, these results are quite contradictory to those previously published by Tidjani and Wilkie. In this study, which is about the flammability and the ageing of PP-g-MAH containing nanoclays, the authors showed that nanoclays enhance the photo-oxidation of the material: absorbance at 1715 cm⁻¹ (related to ketones and carboxylic acids) increases faster and the induction period decreases from 20 hours from PP-g-MAH to 0 hour for nanocomposites. Moreover, the authors did not observe significant and systematic changes of cone calorimeter data after ageing.

Braun et al. [49] have compared the resistance to weathering of various materials. The materials include polycarbonate (PC) or a polycarbonate/acrylonitrile butadiene styrene copolymer blend (PC/ABS) flame retarded with bisphenol A bis(diphenyl phosphate) (BDP) and talc, polyamide 66 (PA66) flame retarded with melamine

cyanurate (MC) and PP flame retarded with various types of intumescent systems based on APP. BDP acts as flame inhibitor and char promoter, MC promotes dripping and fuel dilution. Weathering cycles combine UV-rays (uva-340 nm), temperature (between -20 °C and 70 °C), relative humidity (0 to 5%) during 28 or 84 days. All the samples exhibit changes at their surface after weathering: water permeation, cracks, polymer oxidation, blooming out of flame retardants (talc, melamine cyanurate) or their degradation (orthophosphates are formed from polyphosphates in PP formulations). Nevertheless, the flame retardancy of PC and PA66-based formulations (measured using cone calorimeter) is not modified after weathering. The authors properly claim that the modes-of-action in these systems are bulk properties and are not severely modified by changes occurring into a thin surface layer (however, it must be noted that cone calorimeter is not really suitable to assess the efficiency of dripping promoted by melamine cyanurate).

On the contrary, the PP-based formulations undergo severe degradation of their fire performances after weathering. The first pHRR (corresponding to the degradation of the polymer before the formation of the intumescent char) is mainly impacted and it increases significantly (see Figure 8). As explained above, these results are explained by the degradation of ammonium polyphosphate in orthophosphate and its dissolution/exudation. Therefore the char formation is prevented or at least slowed down. Moreover, the authors properly noted that the decrease in PP viscosity (due to its degradation) can disturb the expansion of intumescent char. In this case, while the flame retardancy is ensured by a surface mechanism, weathering has a strong influence.

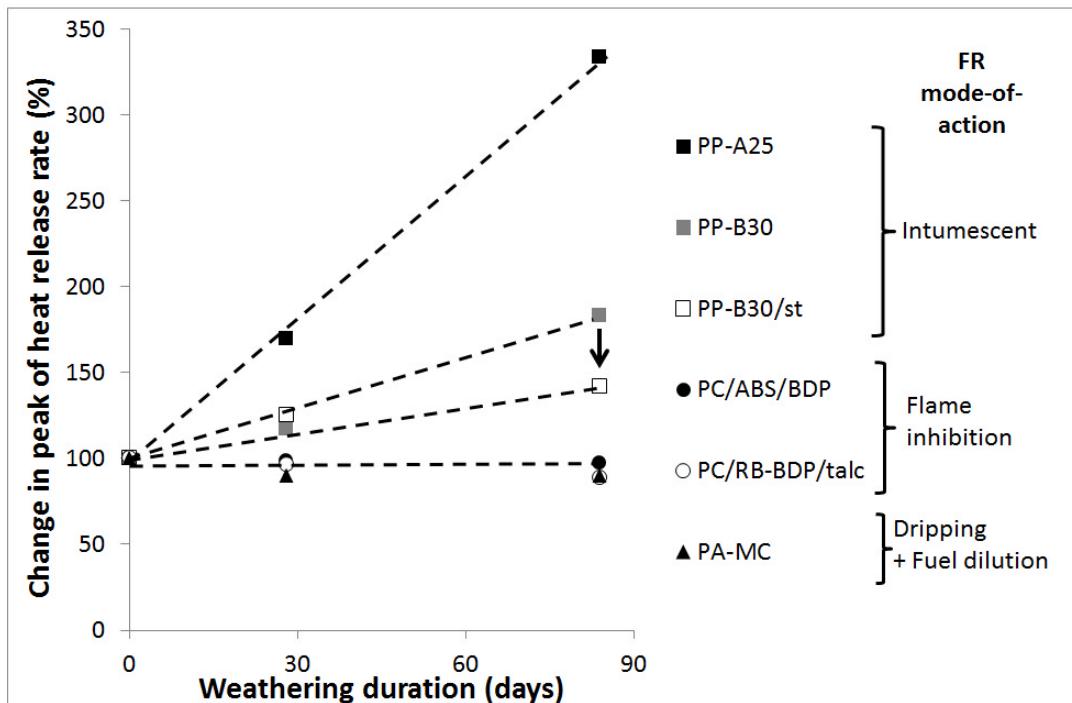


Figure 8 – Changes in pHRR of various formulations (measured in cone calorimeter) versus weathering duration – For PP-based formulations, the values correspond to the first pHRR (graph drawn data in [49])

Most generally, UV ageing is accompanied to other sources of ageing (like heat and moisture). Therefore it is sometimes difficult to identify the main sources of ageing. Hence, Chen et al. [50] observed a strong decrease of LOI and UL-94 rating of PLA/ramie composites flame retarded by APP after several days of weathering combining UV, heat and water/moisture. The detail of ageing conditions are not fully described (intensity of UV irradiation (UV-B313 fluorescent UV lamp): 0.6 W m^{-2} , ageing cycle in two phases: 8 h at $60\pm1^\circ\text{C}$ and 4 h at $50\pm1^\circ\text{C}$, during 7, 14 and 21 days - according to GB/T 16422.3 standards; the exposure to moisture is not specified). But it seems at least that water (and not only UV-irradiation) plays a role in degradation. Indeed, migration of APP to the surface is assigned to its hydrolysis (APP is initially water-insoluble and becomes soluble when its molecular weight decreases). Migration leads to a heterogeneous distribution of APP into the material

resulting in a relatively dense (then little expanded) char layer. Moreover, the covering of fibers by APP is less perfect promoting the candlewick effect.

Nevertheless, the synergistic effect of UV-rays and water seems to be well-established. In the article of Braun et al., dissolution of APP in presence of water explains the degradation of the fire performances of PP flame retarded with intumescence system [49]. Nevertheless, the use of a hindered-amine stabilizer (HAS) allows preventing this deterioration in some extent (see Figure 8, st label corresponds to the presence of a stabilizer). Therefore, it can be assumed that UV radiation also plays a role in the degradation, probably by promoting the cracking of the surface.

A study done by Wang et al. [51] showed that the accelerated ageing (500 h, cycles of water spray and drying, UV-radiation, 50 °C and 70% of relative humidity) negatively affects the efficiency of an APP/pentaerythritol (PER)/Melamine (MEL) system, used as FR coating. Coatings prepared with this system, acrylic resin as binder and some other components were applied to 5 mm thick steel plates and exposed to gas blowlamp flame. The temperature on the backside of the plate was measured using thermocouples. The thickness of the char layer was reduced from 32.5 to 9.7 mm after ageing and the fire-resistant time (time to reach 300 °C) was decreased from 120 to 49 minutes. APP, PER and MEL form a highly intumescence three dimensional phospho-carbonaceous structure (“honeycomb structure”) during burning which imparts very efficient flame retardancy. Ageing damages this “honeycomb” structure and these FRs can only form a disordered uncrosslinked carbon structure. The authors explained that UV-rays can break carbon chains from carbonic agent (PER) and some groups of acrylic resins and ammonium

polyphosphate can crystallize and migrate to the surface when exposed to high humid environment. However no attempt was carried out to evaluate the respective influence of both parameters.

Almeras et al. [52] also investigated the flame retardancy of a PP/polyamide 6 (PA6)/APP/ethylene vinyl acetate (EVA₂₄) blend before and after ageing. EVA₂₄ is an ethylene vinyl acetate copolymer containing 24 wt% of vinyl acetate. Ageing was carried out under a xenon lamp exposure (1.1 W m⁻²) and rain and temperature cycling for 200 h (18 min of wetting and 102 min of drying at 65 °C, relative humidity was 50%). Fire properties were measured using cone calorimeter (irradiance of 50 kW m⁻²), LOI and UL-94 tests. The initial sample exhibits a LOI of 33 and is rated V0 in UL-94 test. After ageing, LOI value decreased to 23 and UL-94 test is not classified. In the cone calorimeter test, the first HRR peak (pHRR) increased from 200 kW m⁻² for the initial sample to 300 kW m⁻² for the aged sample. The ageing leads to the formation of a smaller intumescent protective structure (corresponding to the first pHRR). This decrease in performances after ageing is assigned to the degradation of 21.6 wt% of APP by hydrolysis and to its exudation (or to the exudation of its degradation products: orthophosphates, pyrophosphates and short chain polyphosphates). The water diffusion into the material and the exudation are facilitated by the surface degradation (oxidation and craze). Then the authors assumed that these modifications need the combination of UV and water.

The previous articles have reported that UV-irradiation can induce a decrease in flame retardancy. But other examples may suggest that it is not always the case. Larché et al. [53] have studied the photo-oxidation of crosslinked EVA filled with ATH and kaolin used for cable applications. Photo-oxidation leads to a strong enrichment

of the surface in fillers. The authors excluded the hypothesis of migration and explained this observation by the formation then the release of low molecular weight products due to the EVA oxidation. The composition profile shows that the enrichment occurs in the 350 first microns. In the 100 first microns, the polymer content is less than half of its value in bulk after 500 h of ageing (in SEPAP 12/24 – temperature is 60 °C, irradiance in the range 300-400 nm is 100 W/m²). Flammability was not measured. But the enrichment of the surface would promote barrier effect and improves the flame retardancy. Some works have already shown that EVA filled with mineral fillers exhibited better flame retardancy if these fillers migrate quickly to the surface during a cone calorimeter test [54].

Vilar et al. [55] have also observed nanoparticles (multi-walled carbon nanotubes and silica) enrichment at the surface of PA6 nanocomposites during ageing scenario simulating outdoor application (continuous irradiation - 0.5 W m⁻² - during 1000 hours, 65 °C, relative humidity 50%, wetting and drying cycles). They assigned this phenomenon to the degradation of the matrix. Moreover, the authors have also noted that hydrophilic silica, which are initially well dispersed into the polymer, tend to aggregate. However, it is well-known that the dispersion at nanoscale is a key parameter to improve the flame retardancy of nanocomposites [56]. Therefore, in such cases, a decrease in flame retardancy may be expected.

We have already seen that emissivity is an important parameter. Wu and Yu [57] have investigated the emissivity of a coating based on polyurethane and aluminum particles after weathering (xenon lamps, 550 W m⁻¹ K⁻¹, 65 °C, relative humidity 60%). These conditions correspond to a more classic and less severe scenario than the thermal ageing at high temperatures considered by Hu et al. [23] for very specific

applications. Emissivity increases during ageing from 0.68 to 0.84 after 2000 h of ageing. Several phenomena are involved: the increase of the surface roughness, the permeation of water which leads to higher absorption by itself and oxidation of aluminum particles.

2.5. Ionizing radiation ageing

Some polymers used in special applications such as nuclear power plants receive significant amounts of radiation. Moreover, the quantity of polymer materials is very important in a nuclear plant. For example, insulating materials for wire and cable represent approximately 1,000 to 2,000 km for each nuclear power plant [58]. Moreover, the potential lifetime of a nuclear plant could reach around 80 years [59]. Therefore, it is important to evaluate the influence of ageing and particularly in this case, the influence of irradiation, on fire behavior of flame retarded polymers used in these conditions. Some recommendations are given about cable ageing management and consequences of ageing on flammability by International Atomic Energy Agency (IAEA) [60].

Different types of ionizing radiations can be considered: X-rays, e-beam, γ -rays and α particles. E-beam is low penetrating radiation and probably may not be encountered as source of ageing. But its use as processing method to modify polymers can induce modifications of flame retardant structures. Alpha particles are highly degrading but very low penetrating. On the contrary, γ -rays are highly penetrating and are probably the most significant source of ageing in nuclear power plant.

To the best of our knowledge, few works about the degradation of flame retardant upon ionizing radiation have been reported. But while photodegradation can induce

significant degradation and subsequent release of some flame retardants (see for example the results of Ghanem and Delmani about decaBDE [34]), γ -rays may be able to promote a similar degradation. Morita et al. [61] have γ -irradiated ethylene-propylene-diene rubber containing decaBDE and condensed bromoacenaphthylene (con-BACN). This last additive has polymerizable double bonds and undergoes polymerization during irradiation. In fact conversion occurs during processing (49% of conversion) and increases with radiation dose (64.5% for 218 kGy and 71% for 932 kGy under oxygen atmosphere). Conversion of decaBDE is much lower (0% during processing, and 8% for 932 kGy). The authors have not studied the change in flame retardancy but they observed that decaBDE enhances the changes in mechanical properties after ageing (chain scission in oxygen and crosslinking in nitrogen) while con-BACN enhances crosslinking and prevents chain scission in some extent.

Radiation ageing of flame retarded polymers has hardly been reported. Clough has studied the thermo-radiation ageing of ethylene propylene rubber (EPR) formulations flame retarded with a chlorine-based FR and antimony as synergist [17]. Samples were continuously heated at 100 or 110 °C and γ -irradiated at 0.05 kGy h⁻¹ for 6 months (total dose 20 Mrad, i.e. 200 kGy). The contents of chlorine and antimony decreased during ageing but not faster than with thermal ageing (without radiation exposure). The authors assumed that the “radiation ageing of EPR with respect to the loss of fire-retardant additives is relatively less significant compared with the effects of thermal ageing”. Nevertheless, the formulations submitted to the thermo-radiation ageing were not evaluated using fire tests.

On the other hand, many works have been devoted to modification by irradiation of flame retarded polymers (especially for wire and cable applications). In these studies,

total radiation doses generally did not exceed 100 kGy, i.e. even less than in Clough's study. While modifications by irradiation mainly depend on the total dose, these works can offer an insight about the radiation ageing of flame retarded polymers. Nevertheless, in many cases, additives were incorporated to promote crosslinking of the polymer, which may not be the case when a polymer is submitted to radiation ageing (i.e. during its lifetime).

Irradiation can be beneficial, neutral or detrimental to flame retardancy of flame retarded polymers according to the material and the fire test. For example, Balabanovich et al. [62- 65] have improved the flame retardancy of PA6, PA66 and PBT containing phosphorus FR using a radiation-crosslinking procedure (LOI and UL94 tests). However, cone calorimetry studies generally show an increase in pHRR [66-69].

Change in flame retardancy may be primarily attributed to modification of the polymer. Crosslinking can prevent the expansion of a material containing an intumescent system [70]. Chain scission can lead to small molecules decreasing the thermal stability. Moreover, irradiation may modify the fillers [71] or their dispersion into the matrix [67, 72, 73]. Interactions between crosslinking agent and flame retardant have also been postulated [69]. Nevertheless, all these effects are not proven but only suggested.

Recently, a study has pointed out the influence of heat distortion induced by irradiation on the flame retardancy of a flame retarded PP/PA6 (PP=80 wt% and PA6=20 wt%) blend [74]. The blend containing 1 phr of crosslinking agent (TAIC-triaryl isocyanate) was submitted to various radiation doses (up to 100 kGy) and tested using cone calorimeter. Crosslinked blends (especially at 50 and 100 kGy)

distort severely during the test due to the strong heat gradient through the 4 mm-thick sheet. Nevertheless, no change is observed in the HRR curve in most cases. However, when the flame retardant system (a combination of a phosphorus-based FR- Exolit 1311– and an organomodified MMT- Nanofil 5) promotes the formation of a organomineral protective layer on the sample surface (heat shielding), heat distortion breaks down this layer leading to a strong increase in pHRR even at relatively low radiation dose (20 kGy): 360, 593 and 661 kW m⁻² for radiation doses of 0, 20 and 100 kGy respectively (Figure 9). Measurements of the temperature of the lower surface show that the protective layer is not efficient anymore after cracking. According to these results, flame retardant strategies based on heat shielding should be avoided in case of radiation ageing.

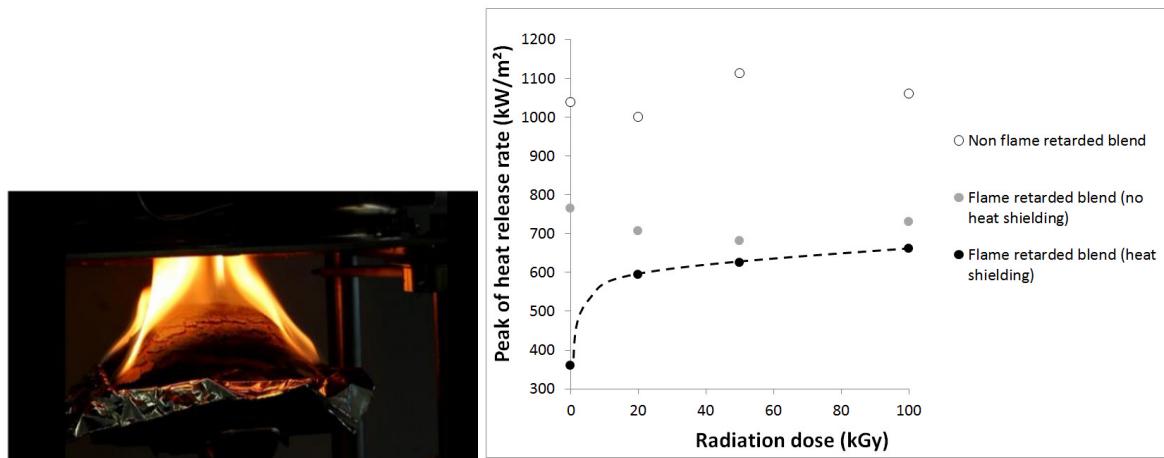


Figure 9 – Heat distortion of a PP/PA6 blend during cone calorimeter test (left) and change in pHRR for three blends with radiation dose (right) - irradiance 50 kW m⁻² (Graph drawn from data in [74])

2.6. Recycling

Mechanical recycling allows polymers to live a second (or more) service life. But recycling is not without consequences for the structure and performances of a material. Therefore it can be considered as an ageing process in some extent. There are some specific problems with the recycling of polymers [75]. First, polymers at the end of their first lifetime have undergone several types of ageing during their service life. Similarly flame retardants may be also aged. Moreover, new processing steps at high temperature (extrusion, injection-molding) can lead to further degradation due to thermomechanical stresses, particularly if anti-ageing additives have already been consumed. Finally, the presence of different polymers and FRs into the waste deposit results in a material containing impurities and/or various additives despite sorting steps. These impurities can increase the flammability and antagonistic effect between different additives can also be expected.

There are few works about the flame retardancy of “real” recycled flame retarded polymers due to their long service life. However, the preliminary remark about the applicability of accelerated ageing tests is particularly relevant in this case. Indeed, ageing conditions during the whole service life can be complex and changing. Therefore, various partially independent phenomena can occur during service life. For example, Brebu et al. [76] have studied a PVC cable waste exposed to the outdoors during 18 years. They observed various modifications due to ageing which could induce changes in flame retardancy: partial dehydrochlorination, oxidation and crosslinking of PVC, consumption of 20 wt% of stabilizers, slight loss of plasticizers (2 wt%) and no loss of fillers (kaolin). Moreover, recycling combines various ageing sources during service life followed by processing steps (another cause of

degradation). Therefore, in the general case, it should be recognized that accelerated ageing is not suitable to assess the modifications undergone by a recycled material.

Contamination is also a great concern for recycled materials. Waste electrical and electronic equipment (WEEE) is currently subjected of many researches while these waste deposits are very complex. Many engineering polymers (mainly styrenics) are mixed, a large waste fraction is black and/or flame retarded with brominated flame retardants which must be removed according to RoHS European Directive [77].

Beigbeder et al. [78] have studied the properties of various plastics sorted by near infrared device from WEEE. While virgin ABS is unrated in UL-94 classification, recycled ABS sorted from the deposit studied by these authors is V1-rated. This result evidences that recycled ABS contains flame retardant additives. When ABS was sorted twice with the same procedure, it became V0-rated which is the best rating. Similarly, its performance increased according to Glow Wire Ignition Test. The sorting procedure did not allow separating flame retarded polymers. Therefore, the best performances after two sorting steps would be assigned to the increase of ABS purity, i.e. to the removal of polymeric impurities among those which are identified and separated by the near infrared device. While purity was as high as 90% after only one sorting step, this study highlights that a small amount of impurities can impart negatively the flame retardancy of recycled plastics.

As stated above, recycling is not only a simple reprocessing: ageing during service life and contamination must be taken into account. Nevertheless, multiple extrusion is quite often used to simulate recycling. Almeras et al. [52] have simulated the recycling of a PP/PA6 blend compatibilized with EVA and flame retarded with APP. The great interest of this work is also to compare two ageing scenario: weathering

(already discussed – see above) and “recycling”. Both scenario lead to a degradation of the flame retardancy. LOI decreases and both pHRR observed on the HRR curve measured in cone calorimeter test increase. Nevertheless, LOI is more impacted by weathering (it decreases from 33 to 23 for the aged material and 27 for the recycled one). The first pHRR increases much more with weathering while recycling is more detrimental for the second one (due to a lower expansion of the intumescent char). Time-to-ignition does not seem to be modified. These differences are assigned to various changes in the composition and the structure of the materials. According to the elementary analysis, recycling does not lead to the migration and exudation of APP or its degradation products, contrarily to weathering. On another hand, according to ^{31}P NMR, 76.6% of APP is degraded after recycling versus “only” 21.6% during weathering. Thermomechanical stresses explain this severe degradation. Moreover, PA6 and APP can start to react during the processing because the temperature of reaction is close to the processing temperature. Finally PP undergoes chain scissions and oxidation.

Imai et al. [79] have studied the recyclability of various commercial flame retarded plastics using multiple reprocessing steps. PC/ABS and PC/hiPS were flame retarded with organic phosphate esters while halogenated compounds (brominated epoxy oligomer or tetrabromobisphenol A) were incorporated into ABS. Initially, all formulations pass the UL-94 5VB tests. But after four extrusion and injection-moulding processes, only brominated materials succeed again. Most of non-halogenated materials fail after only one extrusion and injection-moulding cycle. When samples are maintained at 80 °C and 95% of relative humidity for 168 hours before processing, the degradation of flame retardancy is more dramatic. After one

processing cycle, all non-halogenated materials fail UL-94 test but brominated ABS succeed once again. A common strategy to re-use recycled materials is to mix them with virgin polymers. Even when 30% of recyclate are diluted into 70% of virgin material, non-halogenated materials fail the test. Therefore it can be assumed that halogenated flame retardants are more suitable to warrant flame retardancy after recycling. Nevertheless, polymers used for halogenated and non halogenated materials are not exactly the same. In particular, PC which is sensitive to ageing, was used only for the last ones.

2.7. Miscellaneous

Besides the main sources of ageing discussed above, other situations can be listed. Diffusion of organic solvents into the polymer during ageing must have a huge effect on flame retardancy. Most organic solvents have high heat of combustion, low vaporization temperature and are easily ignitable. While polymers are rather hydrophobic, such diffusion must be relatively easy. Moreover, solvent extraction of additives (including flame retardants) is a particular concern.

Barnes et al. [80] have compared the flame retardancy of various insulated wires before and after ageing in air (100 °C during 7 days) or in oil (100 °C during 24h). All wires passed IEC 332-1 test before ageing. Most of them also passed it after heat ageing in air (except two EVA flame retarded with ATH). Ageing in oil is much severe and 6 of 10 wires failed the test after ageing. The authors have also showed that only halogenated wires (PVC, chlorosulfonated polyethylene and fluorinated ethylene

propylene) passed the test. All other wires (based on EVA, EMA, poly(phenylene oxide polystyrene) copolymer) failed.

We have already reported the work of Ghanem and Delamni [34] about the ageing and release of decabromodiphenyl ether (decaBDE) in backcoated textile samples. In another series of experiences, these authors have compared the release of decaBDE in various extraction media. These media (artificial saliva, artificial sweat and 5% citric acid simulating beverages as orange juice) were chosen to simulate skin or oral exposure. Figure 10 summarizes the results. Obviously, as discussed above, ageing promotes the release of the flame retardant. But all biological fluids are more efficient than distilled water to extract decaBDE, particularly after significant UV or thermal ageing. Nevertheless, it is not possible to assess the influence of this loss of additives to flame retardancy because any fire tests were carried out.

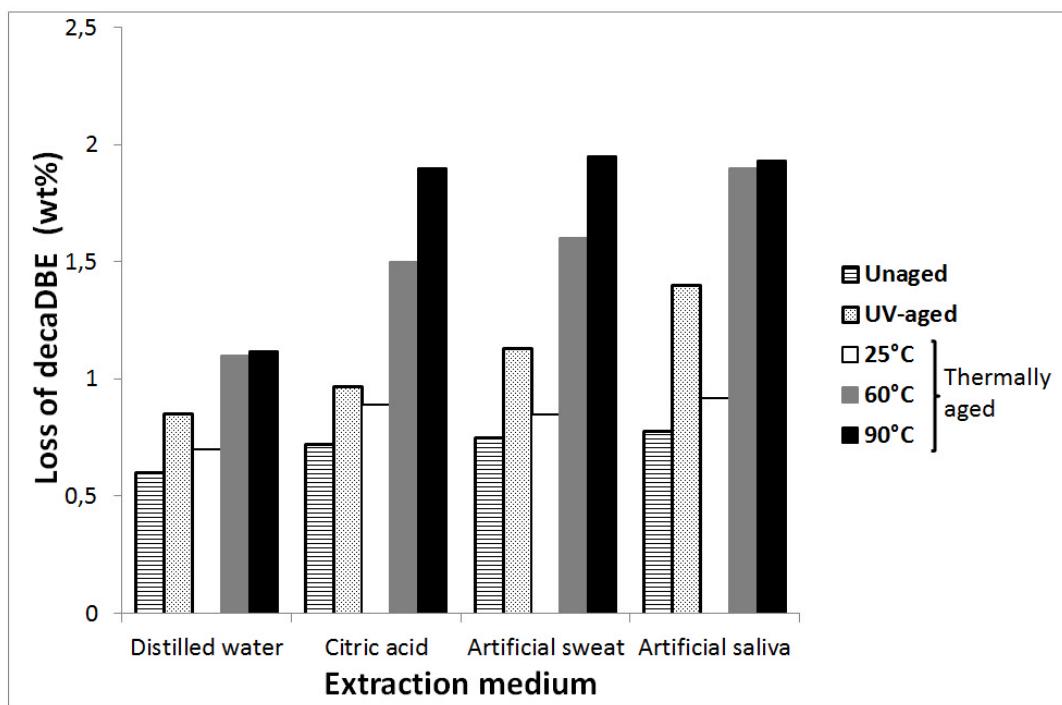


Figure 10 – Loss of decaBDE before and after various ageing scenarii by extraction in different media
(graph drawn from data in [34])

Another study shows how flame retardancy can be impacted by the release of flame retardants. Upholstery covering materials backcoated with fire retardants can be also subjected to domestic cleaning. If materials must legally pass the British Standard BS 5852: Part 1 after a water soak procedure (defined by BS 5651: 1978), it is unclear if this treatment is representative of practical domestic cleaning. Therefore, Yates et al. [81] have established the most popular methods to remove spills and stains on upholstery and used these procedures to clean various flame retarded materials (cotton, acrylic velvet, polyester/cotton). If almost all materials pass the water soak procedure, many of them fail after some domestic cleaning methods including the use of stain removers. Moreover, according to the cleaning method, it is not always the same materials which fail the fire test. The authors assumed that domestic cleaning may adversely affect the efficiency of backcoated flame retardants. The flame retardants were not identified (halogenated are often used in these applications) and their presence after cleaning was not studied. Therefore it is not possible to assess the mechanisms (degradation, migration and removal of FR) in each case. But these results show that it is important to study materials under representative conditions of ageing.

Organic liquids can be detrimental even if they remain at the surface of the material (without diffusing into the bulk). The influence of oily contamination on the flame retardancy of various fabrics was comprehensively studied by Mettananda and Crown [82, 83]. Oily contamination concerns mainly workers in the energy sector, fire-fighting or military. Three fabrics were selected: inherent flame retarded aramid fabric, viscose/poly(amide-imide) blend 50-50 (viscose was flame retarded with 2,2'-oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide Sandoflam 5060) and

cotton/nylon blend 88/12 flame retarded with Tetrakis (hydroxymethyl) phosphonium chloride-urea-NH₃ system. Oil was dropped from a burette onto predetermined spots spread over the fabric surface. Various laundry treatments were also carried out to remove oil. Flame retardancy was assessed using LOI, damage length in CAN/CGSB-4.2 No. 27.10 test and cone calorimeter at irradiance of 75 kW m⁻².

The presence of oil increases the amount of fuel and therefore is believed to increase the flammability. Indeed, all contaminated fabrics ignited faster. In cone calorimeter tests, contaminated fabrics exhibit higher pHRR, Total Heat Release (THR) and Effective Heat of Combustion (EHC). For example, pHRR increases from 200 to around 650-700 kW m⁻² after contamination for the flame retarded viscose/aramid blend.

Nevertheless there is no simple relation between the oil amount and the flame retardancy. Moreover, in some cases, the evolutions of LOI and damage length appear contradictory. The authors explain that not only the oil amount but also its localization (at the surface or in the bulk of fibers) plays a role. When oil is present at the surface (aramid fabric), its vaporization is easy and leads to an increase in flammability. When oil penetrates into the fiber and accumulates in the lumen (cotton/nylon fabric), flammability is less impacted because the oil vaporization is more difficult. Finally, for viscose/poly(amide-imide), flame retardancy is improved for a small amount of oil. The authors suggest that the energy released initially by the oil combustion activates the flame retardant increasing its efficiency. Another explanation is that oil interferes with interactions between poly(amide-imide) and viscose or their degradation products.

For electrotechnical products, a strong fire risk is due to the dielectric breakdown of the polymeric insulation material, leading to arcing. High-temperature arc propagates through the dielectric medium and its temperature (over 6500 K) may induce ignition. This is a specific case where the flame retardancy (i.e. the resistance to ignition) is not determined by typical properties related to pyrolysis or combustion but to a fully different property, namely the breakdown strength (expressed in V/m). This property can be modified under various sources of ageing (thermal ageing, contamination...). Babrauskas [84] has comprehensively reviewed the different factors leading to the ignition of PVC-insulation material.

Among various sources of ageing, electrical ageing leading to voltage-induced degradation of the polymer can be mentioned. Not only moderate continuous voltage but also voltage surges can be detrimental even if the voltage is not high enough to cause direct breakdown. Indeed, ageing promotes the development of arc-tracking leading to arcing after a delay.

As an example, Novak et al. [85] have studied the time-to-failure of PVC-based wires exposed to heat flux (in a modified cone calorimeter). Failure manifested as arcing event. In some experiments, they measured the time-to-failure versus the constant nominal applied voltage (between 20 and 140 VAC) for wires exposed to an irradiance of 50 kW m^{-2} . Arcing occurs faster when voltage increases. Nevertheless, results are highly scattered, maybe due to the stochastic nature of such phenomenon. It must be noted that test conditions correspond to a fire scenario (exposition to high heat flux) and not to a long ageing under moderate conditions.

Mechanical abrasion is also a source of modification for materials. To the best of our knowledge, release of flame retardants due to abrasion or other mechanical processes has been already studied but only from a health point of view [86,87].

Obviously, abrasion should have a strong impact on materials flame retarded by a thin coating. Mechanical erosion would deteriorate the coating and reduce its thickness. Therefore its protective effect would be impaired.

In most other cases, when the compositions of the surface and in bulk are similar, abrasion probably does not change flame retardancy, because the degradation of the surface is not selective (i.e. abrasion reduces the thickness without changing the composition of the material).

Nevertheless, there are few cases where changes in flammability can be expected. First, abrasion promotes hairiness of textiles [88]. However, pilling creates many free fibrils at the surface of the textile leading to early ignition. Bei et al. [89] noted that the ignition of fabrics is dependent on the organization or density of its structure. Bourbigot et al. [90] assume that the decrease of time-to-ignition of PA6 textiles in presence of clays (from 70 to 20s) is mainly driven by the great fibrillation of the yarn. Garvey et al. studied ring or rotor spun yarns of hybride viscose blends. Among various parameters, they considered hairiness has an influence on flame retardancy of fabrics [91].

Another case concerns low-emissivity materials. As already discussed, emissivity is an important parameter influencing ignition. Emissivity depends not only on the nature of the material surface but also on its roughness. A smooth surface enhances reflectivity while significant roughness increases emissivity. Thickness is also influent in the case of thin coating. Hu et al. [24] shows that emissivity of an epoxy-siloxane coating containing aluminum particles is close to 0.15 when thickness is higher than 40 μm but increases quickly for lower thicknesses (0.42 for 10 μm -thick coating).

Abrasion or other mechanical processes can modify the roughness and decrease the thickness and therefore the resistance to ignition of the material.

3. How to limit the influence of ageing on flame retardancy?

The first option is to limit the influence of ageing on flame retardancy is to use stabilizers (thermal, UV stabilizers...). For example, Wang et al. [51] have improved significantly the durability of coating by incorporating nanometric titanium dioxide particles. TiO₂ is well known as anti-UV additive. The properties of the initial coating after weathering have already been reported (see above). With the incorporation of nano-TiO₂ the thickness of char layer and the fire-resistant time are almost unchanged after 500 h of ageing. It must be noticed that the optimized coating contains not only nano-TiO₂ but also layer double hydroxide particles. Moreover, TiO₂ reacts with APP to form titanium pyrophosphate which enhances the char structure. Therefore it is not sure that the enhancement of the durability is only due to the anti-UV properties of nano-TiO₂ particles.

This article points out positive interactions occurring between APP and TiO₂. Other studies also show synergism between flame retardant and stabilizer. Marney et al. [92] have studied a PP flame retarded with 13 parts of tris(3-bromo-2,2-bis(bromomethyl)-(propyl)phosphate (TBBPP). They showed that the UL-94 rating of this material is improved from V2 to V0 with the incorporation of 1 part of N-alkoxy hindered amine light stabilizer (HALS). The authors proved that the synergism occurs through reactions in condensed phase. The stabilizer promotes the decomposition of TBBPP at lower temperature, leading to the early release of high amounts of

pentaerythrityl tetrabromide (PETB) which acts as flame poisoning via hydrogen bromide. It must be noted that such positive interaction has been observed on unaged materials, i.e. before the stabilizer is consumed and modified into non-active species. Therefore, it is not sure that this synergism is still active after ageing.

However, as discussed earlier, reactivity and antagonistic effects between FR and other additives (including stabilizers) can lead in many cases to the decrease in flame retardant efficiency, just after blending and/or during lifetime. In their review, Wilen and Pfaender [44] also discussed various strategies to limit the detrimental effect of flame retardants on the stability. When flame retardants enhance the ageing of a polymer or interfere with stabilizer, it is sometimes possible to inhibit its detrimental effect. Sinturel et al. [37] have shown that tin maleate, as bromine radicals scavenger, helps to reduce the oxidation rate of PP (which is otherwise strongly accelerated by the presence of decaBDE). Filler deactivators or coupling agents help to modify the filler surface, preventing the adsorption of stabilizers. Encapsulation of halogenated compounds allows partially suppress its detrimental interactions with HALS.

A promising strategy is to develop multifunctional additives acting as stabilizer and flame retardant. Commercial molecules as Flamestab® NOR 116 (from Ciba/BASF) is a monomeric N-alkoxy hindered amine claimed as flame retardant for polyolefin fibers or films [93]. In their review Wilen and Pfaender have mentioned several patents about similar molecules

Recently, Aubert et al. [94, 95] have developed several new molecules combining diazene (acting as flame retardant) and N-alkoxy hindered amine moieties. NOR116 acts through the formation of alkoxy radicals promoting chain scissions of

polypropylene. Therefore PP drips away from the flame. AZONOR is believed to be more effective in gas phase by interrupting the combustion. Therefore it is efficient for thin and thick polyolefin specimens. 1 mm-sheet of PP containing 0.5 wt% of AZONOR passes DIN4102 test even after 2000 h of weathering.

It must be noticed that these multifunctional molecules are up to now used at a content typical of stabilizers (i.e. lower than 1 wt%) and are not suitable for applications requiring a high level of flame retardancy. Hence polypropylene containing 0.5 wt% of AZONOR is not UL-94 rating. In combination with classic flame retardants (5 wt% of decaBDE or 30 wt% of aluminum trihydroxide), “only” V2 rating is reached.

Flame retardants can impair the stability of the polymer and the efficiency of stabilizers but other phenomena lead to degradation of the flame retardancy during ageing. Hence, various ageing scenarii, particularly thermal ageing, promote migration and exudation of additives. To overcome these phenomena, several options can be considered. Migration can be limited by the use of polymeric additives (but other problems may arise like the low compatibility and dispersion of such additives with the matrix). Incorporating flame retardants into the polymeric structure or network (strategy called the reactive way versus the additive one) suppresses the migration (at least as the covalent bonding between the FR group and the matrix is not broken during ageing). Moreover, the reactive way is quite often more efficient, particularly to enhance the charring and maintains easier the physical and chemical properties of the material [96,97].

While migration is also driven by the interfacial tension between the additive and the matrix, the use of a compatibilizer can reduce its rate. Almeras et al. have observed

that EVA (with 24 wt% of vinyl acetate) prevents the exudation of APP during processing in PP/PA6/APP blends [98]. Nevertheless, in another article [52], the same team noted that EVA fails to prevent APP exudation during weathering (as already discussed – see above).

Diffusion of water or oxygen as deleterious sources of ageing can be prevented by nanoparticles. Wang et al. [99] reported the ageing of coatings based on APP, melamine and some other components. Coatings were used to protect steel plates. After accelerated weathering (UV radiation, temperature of 50 °C, relative humidity of 70% and cycles of water spraying and drying), the expansion rate decreases (the protective layer thickness decreases from 29.6 mm to 18.9 mm). The fire-resistant time (determined when the temperature of the back surface of the steel plate reaches 300 °C) decreases from 77 to 54 minutes. On the contrary, using 1.5 wt% of nanoclays, the performances remain stable after ageing: the thickness decreases from 32.5 to 27.8 mm and the fire-resistant time is stable (87 and 80 min for initial and aged coatings respectively). This is assigned to the labyrinth effect of the nanoparticle interpenetrating network which prevents the penetration of water. The authors also pointed out that nanoparticles content must be well chosen. The incorporation of 3% of nanoclays leads to poor fire performances due to the low expansion of the char structure.

Encapsulation allows protecting flame retardant against the contact with water. While APP is particularly sensitive to hydrolysis leading to its migration, this strategy was already used, for example by Chen et al. [50]. The poor flame retardancy of PLA/ramie/APP after weathering has already been reported (see above). A microencapsulated ammonium polyphosphate (MCAPP) coated with melamine-

formaldehyde (MF) resin prepared using in situ polymerization with ultrasonication was also used in replacement of APP.

Based on several SEM micrographs, the authors concluded that microencapsulation of APP avoids the migration during ageing. The results of LOI and UL-94 tests show that the encapsulation has a beneficial effect on flame retardancy (Figure 11). LOI does not drastically decrease after ageing for samples containing MCAPP, contrary to the samples containing non-encapsulated APP. The samples containing MCAPP maintained a V-0 rating in UL-94 test even after ageing for 14 days. The investigation after fire tests showed that the char structure of the samples containing MCAPP is not modified and therefore the char can continue to act as an effective protective barrier against heat.

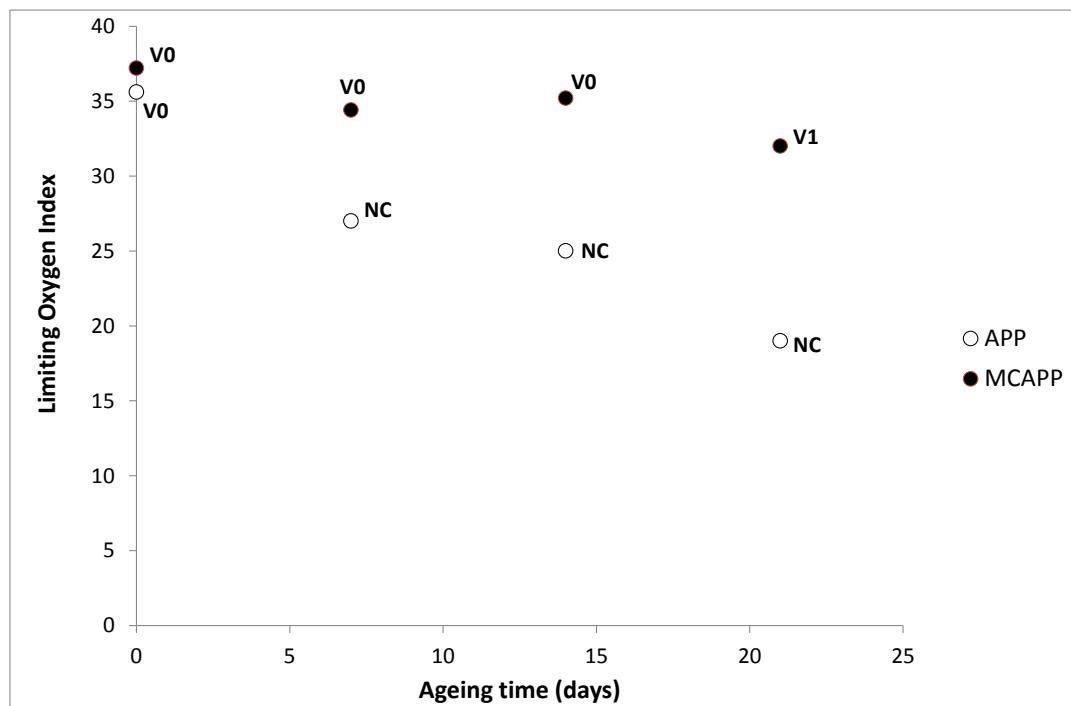


Figure 11– LOI of PLA/ramie/APP and PLA/ramie/MCAPP 59.5/30/10.5 versus ageing time (labels correspond to UL-94 rating) (graph drawn from data in [50])

Wang et al. [100] have also confirmed that microencapsulation of APP is an efficient way to maintain the fire performances during ageing. EVA flame retarded with an intumescence system (containing microencapsulated APP) maintains UL-94 V0 rating after 168 hours of ageing in distilled water at 50 °C. Its limiting oxygen index decreases only slightly from 34.5 to 30.5.

On the contrary, in the work of Braun et al. [49] encapsulation of APP in flame retarded polypropylene was not so efficient to prevent the degradation of the flame retardancy after weathering. As already reported, the weathering leads to a strong increase in the first pHRR (from 99 to 330 kW m⁻² after 84 days) of PP filled with APP. When APP is encapsulated, the first pHRR also increases significantly (from 81 to 225 kW m⁻²). The deterioration is only slightly reduced.

In many cases, deterioration of the flame retardancy is mainly due to the permeation of an aggressive agent (gas, liquid or rays) into the material. The permeation of some of them (oxygen, water, UV-rays) can be prevented using a thin coating. Nevertheless, coating is directly exposed to the radiative heat flux or flame. Therefore it must be flame retarded. If not, it may enhance the flammability. Recent developments in flame retardant coatings have been recently reviewed [101, 102]. In another hand, we have seen that coatings are highly sensitive to various ageing conditions. In other words, coating can be a suitable method to limit the permeation of water, oxygen, UV-rays (which can promote the degradation of the flame retardancy), but it must be flame-retarded and resistant to all kinds of ageing. Some regulations were established by the “European Organisation for Technical Approvals” (EOTA) [103] in order to testing the effect of ageing on flame retardancy of all products containing a “coating system”. EOTA mentioned that “The *fire retardant*

products shall not deteriorate during their assumed intended working life so as to affect the reaction to fire performance of the products. The fire retardant products shall be durable to the conditions in service such as: variations in temperature, variations of relative humidity, rain, radiation from the sun (UV exposure)". The details and conditions of ageing and fire tests are explained in a guideline. It is one of the rare regulations taking into account the effect of ageing on flame retardancy. Developing such durable and flame-retarded coatings is a challenge.

4. Conclusions

There is a significant number of publications about the ageing of flame retarded polymers. But in most cases, no fire tests were carried out. Relatively few works have been performed in order to assess the effect of ageing on the flame retardancy. Therefore, this review is also an attempt to list all phenomena which can lead to a change in flammability even when experimental studies are missing.

Actually, only few scenarios have been extensively studied. Several studies have been devoted to the ageing of polymers flame retarded with decaBDE. Another flame retardant widely studied is ammonium polyphosphate widely used in intumescent systems.

According to the wide range of ageing conditions, polymer and flame retardants, ageing can lead to decrease, no change or even increase in flame retardancy. If major issues may be easily expected (as the solubilization of ammonium polyphosphate in presence of water), flame retardancy is sometimes deteriorated due to unexpected or unpredictable phenomena. Hence, voltage surges are random

events able to reduce significantly the lifetime of wires. Slight migration of plasticizers from inner parts to sheathing was considered responsible for the degradation of the flame retardancy of PVC-based cables. Therefore, not only studies on simple “model” materials need to be carried out, but also experiments on “real” complex materials in ageing conditions the closest to those expected during the service life.

Beyond these specific cases and despite the scarcity of studies, the current literature allows drawing some general comments. In our opinion, two series of conclusions can be listed.

The first one is related to ageing conditions:

- Thermal ageing: The main effect of thermal ageing at moderate temperatures (as occurring in most applications) is migration of additives (not only flame retardants).
- Ageing in presence of water/moisture: Water as degrading agent is often very detrimental for flame retardancy through various chemical or physical phenomena: hydrolysis, degradation or solubilization of some flame retardants promoting migration and exudation, sudden vaporization (when free water is trapped into the matrix) leading to the fast collapse of the material during burning. It also appears that ageing in salt water (i.e. for marine applications) is more severe. Nowadays, a strong tendency is the development of biomaterials. Many of them are easily hydrolyzable aliphatic polyesters. Moreover, hydrophilic natural fibers are believed to replace glass-fiber in composites. Finally water-sensitive phosphorus flame retardants are more and

more used. All these trends should lead to be very careful about the influence of ageing in wet conditions.

- UV exposure: Due to low penetration of UV-rays, only the surface can be aged. If the flame retardancy is ensured by a protective coating or a mechanism involving mainly the thin surface layer of the material, therefore the coating or the material must be resistant to UV. It must be also noticed that UV ageing is generally combined with other ageing sources. Degradation of the surface may not be detrimental by itself but enhances the diffusion of other aggressive agents (such as water).
- Radiation ageing: Considering the variety of phenomena which could occur upon ionizing radiation, much work is needed to document the effect of radiation ageing on flame retardancy.
- Recycling: Recycling increasingly develops in the future. But few works have already done about potential antagonism between various flame retardants while the identification and sorting of polymers containing different FRs is still an industrial challenge. Moreover, anti-ageing additives should be incorporated to avoid further degradation during new processing steps.

The second series of conclusions concerns materials:

- Polymeric matrix: Physical or chemical modification of the matrix (chain scission, crosslinking, water diffusion, contamination) can severely impact the flame retardancy of the material. In some cases, the effect is observed only on flame retarded material but not on non-flame retarded pure polymer.

- Halogenated compounds: Despite their adverse effects on photo-oxidation and stabilization of the host polymer, some works suggest that these molecules allow maintaining a rather good level of flame retardancy during ageing (in comparison to phosphorus compounds especially)
- Phosphorus compounds: These additives, and particularly APP widely used in intumescent formulations, are generally hydrophilic and very sensitive to hydrolysis. Ageing in presence of moisture can dramatically decrease the flame retardancy of the systems containing these additives as intumescent systems. Nevertheless, very few other phosphorus-based flame retardants have been investigated and much work is needed.
- Nanoparticles and mineral fillers: Very few works have been carried out about the ageing of materials flame retarded with this kind of compounds. Even if these flame retardants are not fully harmless, they appear less susceptible to be degraded during ageing. They can also prevent the penetration of aggressive agents (water, oxygen, UV-rays). Their main detrimental impact is probably to accelerate polymer photo-oxidation by adsorbing stabilizers onto their surface.
- Additives: Not only flame retardants but all other additives must be considered to assess properly the influence of ageing on flame retardancy. At least, the fate of stabilizers and plasticizers must be taken into account.
- Coating: Such strategy is highly relevant to impart flame retardancy while limiting the modification of other properties. On another hand, it is probably the strategy the most sensitive to various ageing conditions.

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