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Flame retardant and weathering resistant self-layering epoxy-silicone coatings for plastics

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ABSTRACT

Lowering fire hazard raised by combustible materials such as plastics may be achieved by the use of suitable flame retardant treatments, like fire protective coatings. However, exposure to long-term environmental conditions can cause loss of their functional properties, thus reducing their effectiveness over time. This is why two or three different layers with specific properties (e.g. adhesive, fire retardant and hydrophobic) are generally needed to provide durable fire retardancy. Effective and economical self-layering coatings can be developed to reduce the number of layers without compromising the advantages of the actual system. In this work, the efficiency of applying a silicone based coating to fire retard polycarbonate and the modification of the behaviors of the system, using a mixture of epoxy/silicone resins, a curing agent and either iron oxide or calcium carbonate as fire retardant filler is investigated. Self-stratification and fillers dispersion were evidenced by microscopic analyses coupled with chemical detection, the flame retardant properties using Limiting Oxygen Index (LOI), UL-94, Mass Loss Calorimetry (MLC), Thermogravimetric analyses (TGA) and a tubular furnace, and aging resistance by accelerated thermal, humidity and UV exposure. It appears that the selected fillers have no negative effect on the layering process when introduced from 2.5 to 10 vol.%: perfect stratification is obtained, with the silicone layer being the top layer. The best improvements in terms of fire retardant properties, adhesion and fillers dispersion were obtained by incorporating 2.5 vol.%: V0 rating at UL-94 and 33 and 35 vol.% at LOI with Fe_2O_3 and $CaCO_3$ respectively were measured when a 200 μm wet thick coating was applied. The coating containing iron oxide was unaffected by weathering conditions. Finally, the application of those coatings on polycarbonate allows the formation of a protective barrier which limits substrate/flame mass transfers. It therefore results in (i) a delay of the time to ignition, (ii) the inhibition of the flame spread and of dripping when submitted to a flame, and (iii) a reduction of the combustibility of polycarbonate. A modification of the structure of the silica network formed by the particles which enhances the barrier effect of the silicone-based layer would be the most probable assumption to explain these excellent results.

1. Introduction

Engineering plastics must be flame retarded to meet the strict requirements of legislation in terms of fire risks. Up to now, the most common approach to provide fireproof properties involves incorporation of fire retardant (FR) additives into the polymeric matrix during processing, which is mostly a low cost and fast technique. However, the loading of FR fillers is usually high, which significantly influences the intrinsic properties of the plastic (such as strength and elastic modulus). The second approach consists in the chemical modification of the polymer backbone (modification of a preformed polymer or grafting of

a functionalized monomer for example). Such modifications, usually rather expensive, depend on the matrix to be fire retarded. It could also lead to a change in morphology and physical properties of the bulk polymer. The third approach involves surface modification but it is a quite new approach to fire retard plastics. Recently, it was reported that solvent based and waterborne intumescent coatings can efficiently protect against fire polymer substrates such as polypropylene, polyamide and polycarbonate [1–3]. Such coatings allow concentrating fireproof properties at the surface of the substrate, where they are the most needed. In this way, bulk properties of the material can be preserved, even during its combustion, and attractive esthetics features can

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be combined.

Nevertheless, it has been shown that their effectiveness over time can be compromised when they are exposed to long-term environmental conditions [4]. To overcome this issue, two or three different layers with specific properties (e.g. adhesive, fire retardant and hydrophobic) must be applied. However, the complex formulations, application and processing steps are not always in accordance with industrials requirements (environmental waste generation, pollution, use of excessive amount of energy until a solid film has been produced …). This is why the eco-concept of self-stratification has been developed. This approach can overcome the current issues by allowing the formation, in one step, of a complex multilayer system or gradient coating structures directly applied onto substrates. The properties of this multilayer system are gathered in one coating composition (optimized surface and adhesion properties) while reducing the processing steps, emission of solvents, production costs and also the interlayer adhesion failures. To date, this concept has been applied in various coatings fields (automotive [5], self-healing and anti-corrosive coatings [6,7]…) and started to be considered for fire retardant applications very recently in our group [8,9]. Thus, it opens the door to a real challenge in this field, while favoring an industrial eco-efficient development of products.

Generally, two incompatible resins are required to form a laminated structure after the evaporation of solvent(s) or water. Until recently, studies focusing on self-stratifying coatings mainly dealt with epoxy resin as primer material, and acrylics, alkyds, polyurethanes, polyesters, vinylics or fluorinated resins as topcoat resins [10–13]. We showed in a previous paper that an epoxy/silicone system exhibits perfect stratification and adhesion properties on polycarbonate when diluted in a blend of butylacetate:xylene (1:1), with the silicone phase located in the upper layer of the film after application [14]. Pigments or fillers can however also affect stratification, visual appearance and adhesion properties. Recent studies seem to establish that the use of additives in self-stratifying coatings mainly disfavors the stratification. Indeed, the majority of fillers promotes the compatibility between resins: dispersants, leveling agents, flow control and surface active agents were shown to drastically deteriorate the stratification level [11,15,16].

Thus, the strategy of this study was to find FR additives which can significantly enhance the flame retardant properties of the epoxy/silicone self-layered coating, and therefore of polycarbonate (PC), without affecting the stratification process. First, the applicability of such systems was investigated by incorporating red iron oxide (Fe_2O_3) and calcium carbonate in different amounts (2.5, 5 and 10 vol.%). The interest for those fillers was based on a literature review. First, iron-containing compounds are found to considerably inhibit the combustion and smokes generated during combustion. They are also known as thermal stabilizers and radical recombination catalysts, and are able to absorb UVA [17–26]. However, their effectiveness in non-halogenated systems is being questioned [27–29]. Then, calcium carbonate ($CaCO_3$) has been widely studied as a non-flammable halogen free FR within a large range of polymers, copolymers and propellants [30–32]. Recently, its use in silicone matrix was a central focus: the incorporation of precipitated $CaCO_3$ in a silicone matrix can increase its thermal stability [33,34]. To date, numerous studies have also been conducted with the aim of using $CaCO_3$ to dilute the amount of fuel to be consumed [35].

In the light of those facts, the effects of iron oxide and calcium carbonate additives on both the stratification process and on the flame retardant properties of the epoxy/silicone self-stratified coatings will be studied in this paper. Finally, the weathering resistance of the most promising systems will be investigated.

2. Experimental

2.1. Materials

Based on previously published results [8,14], two commercial resins

were chosen: an epoxy (Bisphenol-A epoxide, Sigma–Aldrich, St. Louis, MO, equivalent weight: 172–176, 100% solids), a silicone (a phenyl branched resin containing 6% of hydroxyl group from *Dow Corning*, Seneffe, Belgium), as well as a curing agent: polyamine (diethylene triamine (99%), Sigma–Aldrich, St. Louis, MO). Solvents, i.e. M-xylene (99%) and butylacetate (BuAc, ≥99.5%) from Sigma–Aldrich (St. Louis, MO), were used without any purification.

Red Iron Oxide (average particle size 0.30 μm) from Grolman (Cathaycoat Red RA11A, Brno, Czech Republic) and calcium carbonate (average particle size 70 nm, Socal 31, Solvay, Oudenaarde, Belgium) were chosen as fillers.

Transparent polycarbonate (Lexan, 1 mm-thick for microscopic analyses and 3 mm-thick for fire testing) was supplied by *Polydis* (Ligny Le Chatel, France).

2.2. Coatings: preparation and application

To formulate the systems, each resin was first dissolved at 30% wt./wt. in a blend of BuAc:xylene (1:1), they were then mixed and thoroughly stirred at a 1:1 (epoxy:silicone) ratio by weight. When applicable and before the addition of the hardener, fillers were separately dissolved in the epoxy medium. They were grinded at 1200 rpm until a Hegman gauge fineness value of at least 7 was obtained. The hardener was then added dropwise to the system with respect to the epoxy number and mixed for 3 min before coating application. Coatings were applied on PC by using a regular spray gun *Devilbliss* (air pressure = 200 kPa) to obtain a wet film thickness of 200 μm. The coating was dried for 24 h in an oven, and then cured in an oven for 2 h at 110 °C. The dried films obtained were then characterized and tested.

2.3. Characterization of film properties

Microscopic analyses coupled with X-ray mappings (SEM-EDX) were used to identify the coating layers and cross-hatch cutter test was carried out to evaluate adhesion. Fire behavior was evaluated using Limiting Oxygen Index (LOI), UL-94 and Mass Loss Calorimetry (MLC). The most promising specimens were then analyzed either by Thermogravimetric Analysis (TGA) or using a tubular furnace. Residues obtained were then observed using a numerical microscope. Finally, accelerated aging tests were performed and the evolution of film properties and fire performances versus aging were followed. All testing apparatus and conditions used are described hereafter.

2.3.1. Microscopic and spectroscopic analyses

To facilitate cross section analyses, coatings were first cut in liquid nitrogen. Samples were carbon coated before any characterization. SEM-EDX analyses were respectively carried out at 5.0 kV, 20 μA and 13.0 kV, 25 μA on a Hitachi S4700 (Tokyo, Japan) with field emission gun. It was used both for the detection of the layering and the evaluation of the film thickness.

Numerical pictures of residues obtained after fire tests were taken using a microscope VHX-1000 from Keyence (Osaka, Japan, 20×), which allows creating a 3D picture based on automatically captured images.

Molecular structure of polycarbonate, epoxy/silicone coated sample, iron oxide filled, and calcium carbonate filled samples were determined via Raman spectrometer (HORIBA, XploRA TM PLUS) equipped with a confocal microscope (< 1 μm *XY*, < 2 μm *Z* resolution). Raman spectra were recorded with near-infrared (785 nm, CLS high brightness laser, 150 mW laser power) excitation under the ambient atmosphere. The scattered photons were focused onto an air-cooled charge-coupled device (1024 × 256 pixels). The spectral acquisition times were 5 scans accumulated with 10 sec/scan.

2.3.2. Classification of stratification

The classification of stratification was performed following the Brite

Euram Project guideline [11]. It ranks the degree of stratification from 1 to 4 according to the SEM cross section pictures. From this classification, a type I ranking means that a perfect stratification is obtained (e.g. well distinct and homogeneous layers); a type II coating means that a concentration gradient between the two resins can be observed through the film thickness; the type III structure corresponds to the formation of spherical particles rich in one of the resins dispersed in a medium enriched with the other resin, and finally a type IV corresponds to the presence of large parts mainly composed of one of the resins.

2.3.3. Adhesion testing

ASTM D3359-97 standard was followed to evaluate the adhesion of the coatings on polycarbonate using an Elcometer 107 Cross Hatch Cutter test (6 mm × 3 mm cutter blade). A pressure-sensitive tape is applied and removed over cuts made in the film, and according to the specimen obtained, adhesion is classified from 0B to 5B, 0B corresponding to the worst adhesion and 5B to the best.

2.3.4. Fire testing

Limiting oxygen index (LOI: the minimum oxygen concentration needed to support the candle like combustion of plastics) was evaluated using a Fire Testing Technology instrument on specimens (100 mm*10 mm*3 mm) following the standard ISO 4589-2 test.

The UL-94 classification was obtained on barrels (100 mm*10 mm *3 mm) following a standard test (IEC 60695-11-10), i.e. in a vertical position (the bottom of the sample is ignited with a Bunsen burner). This test provides a qualitative classification of the samples, from V0 (best ranking, corresponding to short burning and no dripping of flaming particles) to NC (non-classified, i.e. a burning lasting more than 30 s or up to the holding clamps at 100 mm from the ignition point).

A FTT (Fire Testing Technology) mass loss calorimeter (MLC) was used to carry out the measurements following the procedure defined in ASTM E906. The protocol consists in exposing horizontal samples measuring 100 mm*100 mm*3 mm to an external heat flux of 35 kW/m^2 (developing fire) or 50 kW/m^2 (fully developed fire), with a forced ignition. The surface of the sample is exposed to the heater at a distance of 35 mm from cone base, on a ceramic backing board. Heat release rate (HRR) as a function of time, time to ignition (TTI), peak of heat release rate (pHRR), total heat release rate (THR) and time of flameout (TFO) were evaluated. The experiments were carried out three times to evaluate repeatability, and the data reported are the average of the three experiments. Values are reproducible within a relative standard deviation of ± 10%.

2.3.5. Thermal stability

2.3.5.1. Thermogravimetric analysis (TGA).
A Discovery TGA (TA Instruments) was used. 10 mg of resins, fillers or dry grounded coatings samples (which underwent the same treatment than the coatings) were put in alumina crucibles before experiments, and TGAs were carried out under nitrogen (50 mL min^{-1}). Samples first underwent an isotherm for 120 min at 50 °C to remove any trace of oxygen, and then a heating ramp from 50 to 800 °C at 20 °C min^{-1}. Samples were tested twice to ensure repeatability of the results.

2.3.5.2. Heat treatments and characterization of the heat treated residues.
TGA experiments enable to define characteristic temperatures of degradation of the studied systems. According to the data obtained, heat treatments of raw materials (filled and unfilled) were realized in a tubular furnace under nitrogen flow (75 mL min^{-1}) for 3 h at these chosen temperatures. The collected residues were then analyzed using a numerical microscope.

2.3.6. Weathering resistant properties

PC is sensitive to light radiations and to the contact with hot water, which causes hydrolysis and chemical breakdown [36]. Changes in visual appearance can be noticed after a couple of days under QUV-A

exposure. In this regard, an aging duration of 8 weeks was considered. Accelerated aging tests were carried out on barrels for LOI and UL-94 tests, and plates for visual analysis, color measurements and adhesion testing. Experiments were performed every two weeks and the total duration of the aging was 8 weeks. Before testing, samples were dried for 24 h in a vacuum chamber at 60 °C in order to avoid the excess of humidity and to make all characterizations in similar conditions. The changes in properties of aged materials compared to unaged ones were compared for each period.

2.3.6.1. Temperature and UV (UV) tests.
QUV-A weathering was chosen to simulate the effect of real sunlight in order to provide excellent simulation of sunlight in the critical short wavelength region and to be the most discriminating compare to QUV-B that can produce anomalous results. This experiment was realized by exposing samples simultaneously to temperature and UV rays. For this purpose, a Q-Lab weathering chamber (QUV/se: UV, condensation and control irradiance SOLAR EYE) was used. The weathering conditions were chosen following ISO 4892-3 standard [37]. The chamber contains 8 UV (UVA 340) lamps of 0.89 W/m^2 irradiance. 4 h UV irradiation at 60 °C were followed by 4 h in the dark at 50 °C. The samples were fixed to the test panel and submitted to these cycles without any interruption. The side of the barrel exposed was changed every week to obtain a uniform exposure of each side during aging cycles.

2.3.6.2. Temperature/Relative humidity (T/RH) tests.
Uncoated and coated polycarbonate samples were aged in a humidity chamber (HCP 108, Memmert). Temperature and relative humidity were fixed at 60 °C and 75%, respectively.

2.3.6.3. Color change evaluation.
To evaluate color evolution during weathering, $L*a*b*$ measurements [9] were carried out on the samples before and after aging. Color changes and reflectance were registered with a Datacolor CHECK 3 portable spectrophotometer (Datacolor Industry). In the CIE ("Commission Internationale de l'Eclairage", or International Commission on Illumination) $L*a*b*$ system, $L*$ represents the lightness of color ($L* = 0$ for the absolute black, $L* = 100$ for absolute white), the $a*$ value indicates the color position between red and green ($a*$ is green at one extremity ($a* > 0$) and red at the other ($a* < 0$)) and the $b*$value represents the color position on a yellow/blue scale ($b* > 0$ for blue and $b* < 0$ for yellow). $a*$ and $b*$ values are close to zero for neutral colors (white and gray) and increase in magnitude for more saturated or intense color (pure color). The difference in color (ΔE) allowing comparing two objects is determined following Eq. (1), with $\Delta L*$ the lightness difference and with $\Delta a*$ and $\Delta b*$ the changes in $a*$ and $b*$ values respectively.

$$\Delta E = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2}$$
(1)

3. Results and discussion

In a previous paper [14], we demonstrated that a type I stratification was obtained using a epoxy/silicone blend with BuAc:xylene (1:1) as solvent, and the resulting coating showed an excellent adhesion at cross-hatch test (5B) on polycarbonate.

The aim of the present study is to design, based on this epoxy/silicone formulation, new flame retardant self-layering coatings by incorporating FR additives which do not impact the stratification behavior of the system and have excellent weather resistant properties. To do so, the previously designed systems were tested, by incorporating different amount of fillers, and compared to raw PC and to PC coated with the unfilled system.

Table 1
Fillers location, esthetics of the coating, adhesion rating and stratification pattern resulting from the epoxy/silicone coatings filled with Fe_2O_3 and $CaCO_3$ at 2.5, 5 and 10 vol.%.

Additive	vol.%	Filler location after film formation	Esthetics of the coating	Thickness (μm)	Cross hatch testing	Stratification pattern
No filler	0	–	Slightly rough, glossy	55	5B	I
Fe_2O_3	2.5	Silicone layer	Smooth, good fillers dispersion	32	5B	I
	5			42	5B	I
	10			30	4B	I
$CaCO_3$	2.5	Interface epoxy/silicone & silicone layer	Rough, good fillers dispersion	32	5B	I
	5	In both phases		45	4B	I
	10	Silicone layer		55	4B	I

3.1. Self-stratification study of filled systems with Fe_2O_3 and $CaCO_3$

Coatings containing 2.5 (i.e. 10 wt.% for iron oxide and 2 wt.% for calcium carbonate), 5 and 10 vol.% of iron oxide or calcium carbonate were designed and characterized. Iron oxide and calcium carbonate were initially dispersed in the epoxy phase. The esthetics of the designed coatings, their adhesion on PC, thickness and stratification pattern are detailed in Table 1. The filler location after curing is also reported.

When the formulation contains Fe_2O_3, stratified films with nice visual appearance were obtained, whatever the amount of fillers introduced. At the highest concentration, adhesion begins to be slightly constrained: 4B rating is obtained, compared to 5B with 2.5 and 5 vol. %. In all cases, iron oxide migrates in the silicone layer during curing, as observed in Fig. 1a.

With $CaCO_3$, it was less easy to thoroughly disperse the fillers in the epoxy resin and to properly adjust the parameters of the spray gun to obtain a nice coating. If the filler grinding time is too short, settling is well noticeable even before the mixing with the second resin. However, after these adjustments, coatings with a nice visual appearance and with type I stratification pattern were obtained for all formulations. Adhesion is slightly reduced with 5 and 10 vol.%: a 4B rating is obtained compared to 5B with a lower amount of fillers.

The distribution of calcium carbonate through the thickness is not the same depending on the amount of filler incorporated: it can be present at the interface of both layers (2.5 vol.%), in both phases (5 vol. %) or in the silicone layer only (10 vol.%) (Fig. 1b).

To conclude, iron oxide and calcium carbonate do not affect the layering process when incorporated up to 10 vol.%: they mostly migrate, with a concentration gradient more or less pronounced, to the air interface with the silicone resin. The distribution of $CaCO_3$ through the

thickness is more uncertain. However, it does not impact the quality of the layering: fillers are not well wetted in the resins but they do not modify the equilibrium between the two media.

Question addressed was then if the incorporation of the fillers has an effect on the molecular structure of the coatings. The Raman spectroscopy technique has been extensively used for identifying molecular structure of metal oxide and composite materials. The near-IR Raman (785 nm) spectra of the polycarbonate, epoxy/silicone coated, iron oxide filled, and calcium carbonate filled samples are presented in Fig. 2. The polycarbonate spectrum contains strong and sharp peaks which are assigned to phenyl ring vibration (~ 635 and $\sim 1604\,cm^{-1}$), C–H bending mode (~ 703, ~ 734, $\sim 1002\,cm^{-1}$), O–C(O)–O stretching ($\sim 888\,cm^{-1}$), and C–O–C stretching (~ 1111, ~ 1178, ~ 1236, and $\sim 1294\,cm^{-1}$) mode [38]. In the case of the epoxy/silicone coated samples, most peak positions are very similar to the polycarbonate ones, while some peaks' intensity was decreased (e.g., $\sim 1294\,cm^{-1}$ and $\sim 1450\,cm^{-1}$). This result indicates that coated epoxy/silicone materials did not change the chemical structure of the polycarbonate.

In the case of the calcium carbonate filled sample (position 1), the obtained Raman spectrum is almost identical to that of the epoxy/silicone coated sample. However, the Raman spectrum of the position 2 in which small cluster is clearly shown provides the evidence of calcium carbonate. The new Raman peaks at $\sim 278\,cm^{-1}$ and $\sim 1083\,cm^{-1}$ can be assigned to lattice vibration and C–O–C stretching mode, respectively, of calcium carbonate [39]. Iron oxide filled sample's Raman spectrum at position 1 is very similar to that of epoxy/silicone coated one, except for the $\sim 1002\,cm^{-1}$ peak intensity. In the case of position 2, several new peaks appear at ~ 290, ~ 408, and $\sim 607\,cm^{-1}$ which are evidence of the presence of iron oxide crystal phase [40–43]. Although we can't provide clear explanation of increasing intensity of C-H bending mode at $\sim 1002\,cm^{-1}$ with addition of iron oxide, the
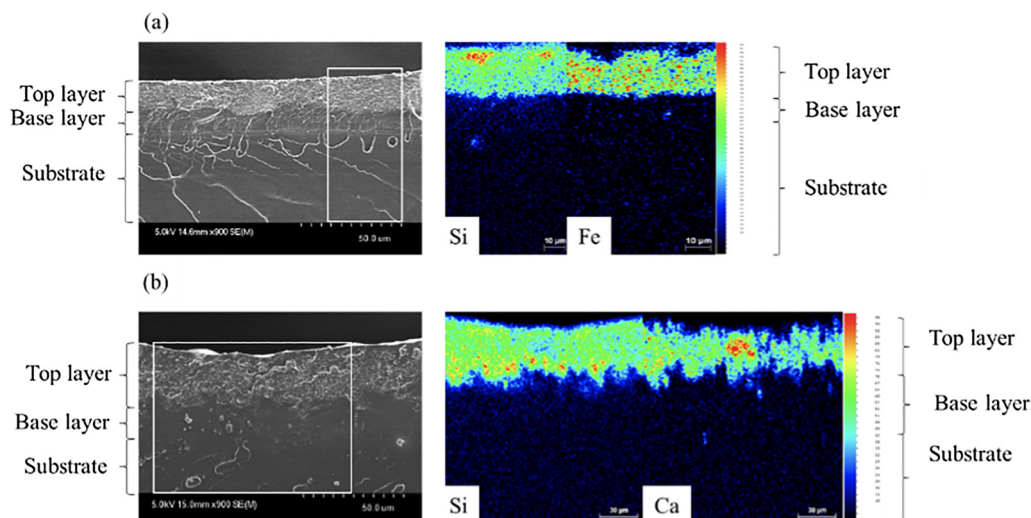
Fig. 1. EDS X-ray mappings of Silicon, (a) iron and (b) calcium on a cross-section of an epoxy/silicone coating filled with 10 vol.% of (a) iron oxide and (b) calcium carbonate.
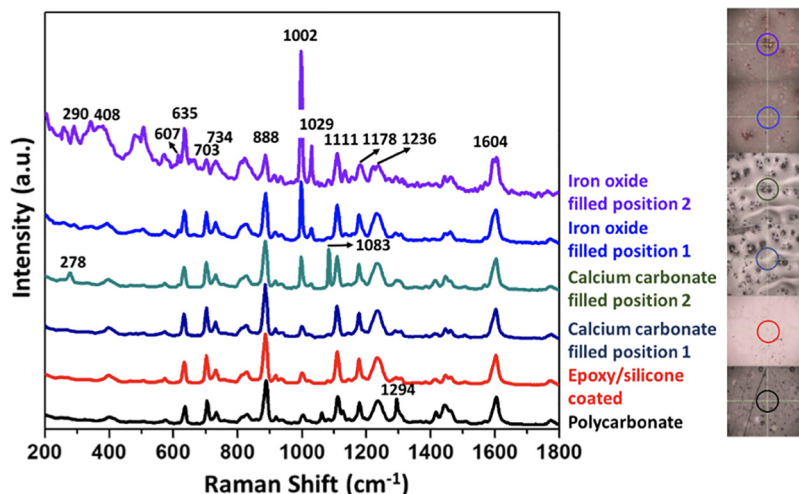
Fig. 2. 785 nm near-IR Raman spectra of the polycarbonate, epoxy/silicone coated, iron oxide filled, and calcium carbonate filled samples under ambient conditions.

observed results indicate that filled iron oxides were well dispersed in the silicon resin without changing of epoxy/silicone structure. The specific differences between each Raman spectra collected in different positions for both the Fe_2O_3 and $CaCO_3$ confirm that both species migrate toward the interface between the silicone resin and air and that they tend to accumulate in small clusters.

As a type I pattern was obtained for all samples, they were tested to evaluate their flame retardant properties.

3.2. Flame retardant properties

Virgin PC and PC coated with the filled or unfilled epoxy/silicone systems were tested for fire performances (MLC, LOI, UL-94) and the mode of action of the coatings to protect polycarbonate was investigated by TGA and using a tubular furnace.

At first, samples were tested at 35 kW/m^2 under MLC. Results are not presented as no ignition of the coated samples (filled and unfilled) occurred at 35 kW/m^2 (mild fire scenario), even after 30 min of exposure; on the contrary to the raw PC which ignited after 319 s and released a total heat of 35 MJ/m^2 (with a pHRR of 202 kW/m^2). Considering this excellent result at 35 kW/m^2, experiments were then conducted at 50 kW/m^2.

Table 2

MLC (50 kW/m^2), LOI and UL-94 values of the uncoated and coated PC with the unfilled epoxy/silicone mixture.

		Virgin PC	Coated PC
MLC	TTI [s]	92 ± 6	148 ± 7
	pHRR [kW/m^2]	231 ± 6	176 ± 4 (−24%)
	THR [MJ/m^2]	52 ± 1	41 ± 3 (−21%)
	TFO (s)	1077 ± 47	903 ± 6
LOI (vol.% O$_2$)		27	28
UL-94		NC	NC

3.2.1. Fire retardancy of the unfilled system

HRR curves and characteristic MLC parameters obtained under a 50 kW/m^2 heat flux are depicted in Fig. 3 and Table 2.

Results clearly evidence an improvement of the fire performances after coating of PC with the epoxy/silicone mixture: both the pHRR and THR are reduced, respectively by 24 and 21% compared to raw PC. In
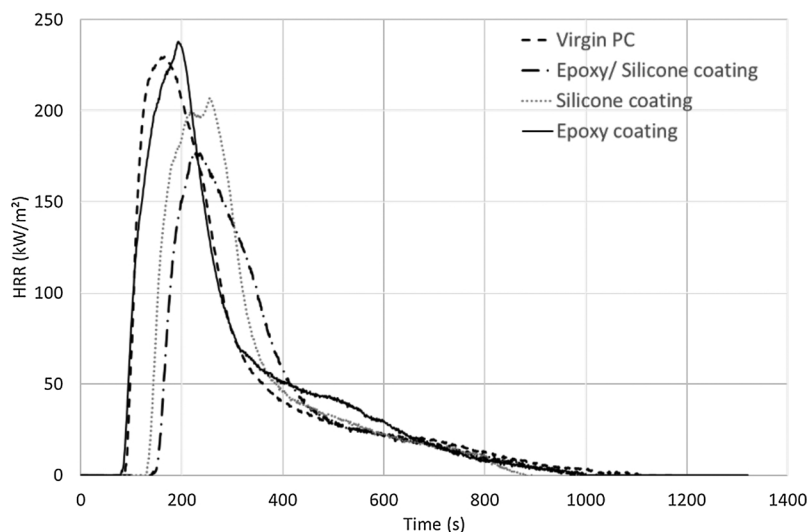

Fig. 3. HRR curves obtained with uncoated PC and coated PC with the self-stratified epoxy/silicone coating, the epoxy coating and the silicone coating solely.

addition, the coating allows a 50 s delay of the ignition time, which is remarkable with such thickness (55 μm). The coating protects temporarily the PC: it swells under the coating, which progressively delaminates from the corner of the plate due to the uprising of the PC char. Then, ignition occurs and the PC forms a char which rapidly goes up to 8 cm. The char is then consumed and collapses before the flame out takes place.

The experimental conditions during UL-94 and LOI testing differ from those of MLC test in terms of fire scenario: MLC is a radiative heat flux test whereas during LOI or UL-94, a flame is applied on a specimen. Different phenomena are therefore occurring during combustion, and so the properties measured can induce different and complementary conclusions compared to those of MLC.

PC is a combustible self-charring polymer (i.e. after its ignition, it progressively melts and builds a char which then degrades at high heat fluxes) and thus reaches a quite high intrinsic LOI value (27 vol.% at 3 mm) compared to other common thermoplastics. The intrinsic flame retardant properties are not improved in the case of vertical burning tests after the application of the epoxy/silicone coating: close LOI values (27 and 28 vol.% respectively for the raw and coated PC) and a non-classified (NC) rating are obtained with both samples. Up to 28 vol. %, the extinction of the virgin PC occurs mainly because of flaming drops or consumption of the material. The coating however allows reducing the consumption speed of the material and retains somehow the flaming drops from falling down. Virgin PC is NC at 3 mm, however close to meet the requirements of V2 classification (short combustion time – 30–40 s – and dripping occurs with no ignition of the cotton). The coated polycarbonate is still NC, although the system behaves differently: the combustion time is nearly zero after the first ignition, but is longer after the second ignition. Moreover, the tendency for dripping is less marked.

Thin silicone-based coatings were already proven to improve fireproofing properties of PC via the formation of an expanded coating upon flaming [44]. Looking at the HRR curves when the PC is coated by the sole epoxy or sole silicone resin confirms the fire retardant effect brought by the silicone resin itself (Fig. 3, Table 3): when the epoxy resin is applied on PC, no delay of ignition is observed compared to that of virgin PC. Finally the epoxy resin does not bring any fire retardant effect, which is not surprising as it is composed of Bisphenol A (as PC itself) but it contributes to bring better adherence between the self-stratifying coating and the PC compared to the silicone coating alone (3B rating compared to 5B with the self-stratifying coating and no interlayer adhesion failure appears between the epoxy and the silicone layers).

The PC samples coated with filled coatings were then tested using the same fire tests.

3.2.2. Fire retardancy of the filled systems

The FR performances of the polycarbonate coated with epoxy/silicone/Fe_2O_3 and epoxy/silicone/$CaCO_3$ systems were then evaluated by LOI, UL-94 and MLC.

LOI and UL-94 data and resulting specimens after testing are depicted in Table 4.

Table 3
MLC values obtained with uncoated and coated PC with the epoxy/silicone self-stratifying coating, the epoxy and the silicone coating solely.

	Coated PC		
	Epoxy/Silicone self-stratifying coating	Epoxy coating	Silicone coating
TTI (s)	148	80	131
pHRR (kW/m^2)	176 (−24%)[a]	238 (+3%)	206 (−11%)
THR (MJ/m^2)	41 (−21%)	53 (+2%)	45 (−13%)

[a] Percentages represent the difference compared to the virgin PC

Filled coatings exhibit outstanding flame retardant performances compared to the raw PC and the unfilled coated PC, whatever the type of filler. When 2.5% of Fe_2O_3 is incorporated, a 5 vol.% increase of the LOI value and the best rating at UL-94 (V0) are achieved. The addition of a higher amount of filler further increases the properties: a V0 rating and 37 vol.% at LOI testing is reached with an addition of 10 vol.%.

When $CaCO_3$ is added to the epoxy/silicone system, LOI values are increased up to 36 vol.% (7 vol.% increase with both 2.5 and 5 vol.% and 8 vol.% increase with 10 vol.%) and the best rating (V0) at UL-94 is also reached.

A change in the fire behavior of coated PC is also noticeable visually due to the addition of fillers: no dripping is observed during both tests, ignition of the samples is considerably delayed and the combustion time is shortened compared to that of the unfilled systems. At UL-94, self-extinguishment occurs less than 6 seconds after ignition, and the resulting char is mainly formed at the beginning of the flame application. During these vertical flame tests, charring is more pronounced for the filled systems (whatever the type and amount of filler) and occurs quicker after ignition than for the unfilled ones. Presence of fillers also prevents dripping to occur and flame spread is much slower than the one observed when raw PC and unfilled coated PC are exposed to the flame.

The HRR curves of both systems exposed to a 50 kW/m^2 heat flux are shown in Fig. 4 and MLC data are reported in Table 4.

When iron oxide is incorporated in the epoxy/silicone self-stratified system, it influences mainly the TTI. With 2.5% of filler, the TTI is comparable to that of the unfilled coated PC but when 5 and 10% of Fe_2O_3 are incorporated into the formulation, two TTI are registered: 26 s and 87 s for 5% and 13 s and 237 s for 10%. The first value is meant to a flash and reflects the difficulty of the coating to ignite. This effect is particularly evident for the system containing 10% of iron oxide as it takes a longer time (237 s) for the sample to ignite again. The presence of remaining solvent in the coated film is probably responsible for the shoulder observed between 10 and 50 s: BuAc and xylene evaporate as soon as they undergo the radiative heat flux due to their low boiling temperature.

With 2.5% of iron oxide, the TTI is comparable to the one of the unfilled coated PC, whereas adding 2.5% of calcium carbonate allows delaying significantly the TTI (189 s versus 148 s for unfilled coated PC). When 5% of $CaCO_3$ is incorporated, two TTI can also be noticed (48 and 139 s for 5% $CaCO_3$) reflecting, as it was observed with iron oxide, the difficulty of the coating to ignite. Contrary to iron oxide, adding 10% of calcium carbonate does not promote the delay of the ignition time.

For both fillers, once the filled system re-ignites, the enhancements in terms of heat release rate are negligible and are even lowered by the incorporation of the fillers compared to the unfilled coated system. No significant improvement is obtained in terms of pHRR and THR with both fillers during the combustion compared to the unfilled coated PC and to the raw PC.

Finally, the unfilled epoxy/silicone coating allowed improving the FR properties of the PC by shifting the time to ignition (+56 s) and decreasing the heat released during the combustion. The addition of fillers (i.e. iron oxide and calcium carbonate) brought additional properties in the presence of a flame: dripping is avoided during the combustion and also flame propagation. The best improvements, combining excellent flame retardant properties, adhesion and fillers dispersion, were finally registered with the systems containing 2.5 vol. % of iron oxide and calcium carbonate: V0 rating at UL-94 was reached and LOI values of 33 and 35 vol.% respectively were measured when a 200 μm wet thick coating is applied. These results show that the FR performances are induced by complex mode of action of the fillers and of the epoxy/silicone system by itself, in condensed phase and maybe in the gas phase too.

The next section is therefore devoted to the investigation of how the silicone-based coatings act to reduce the flammability of PC. To achieve

Table 4
MLC (50 kW/m^2), LOI and UL-94 values of the uncoated and coated PC with the unfilled and filled epoxy/silicone mixtures.

Filler (vol.%)		Coated PC	Epoxy/Silicone/Fe$_2$O$_3$			Epoxy/Silicone/CaCO$_3$		
		0	2.5	5	10	2.5	5	10
MLC	TTI [s]	148 ± 7	141 ± 20	87 ± 5	237 ± 100	189 ± 18	139 ± 57	42 ± 2
	pHRR [kW/m^2]	176 ± 4 (−24%)	205 ± 20 (+16%)	197 ± 1 (+12%)	218 ± 22 (+24%)	241 ± 7 (+37%)	208 ± 7 (+18%)	192 ± 18 (+9%)
	THR [MJ/m^2]	41 ± 3 (−21%)	47 ± 2 (+15%)	51 ± 1 (+24%)	49 ± 7 (+20%)	47 ± 2 (+15%)	45 ± 8 (+10%)	47 ± 3 (+15%)
	TFO (s)	903 ± 6	1003 ± 33	889 ± 4	990 ± 100	1544 ± 76	1010 ± 24	1021 ± 60
LOI (vol.% O$_2$)		28	33	34	37	35	35	36
UL-94		NC	V0 No dripping	V0 No dripping	V0 No dripping	V0 No dripping	V0 No dripping	V0 No dripping

this, different tests were performed to understand their mode of action.

### 3.2.3. Flame retardant effects of iron oxide and calcium carbonate in a silicone-based system

From the fire tests, it seems that the epoxy/silicone coating allows forming a protective barrier at the surface of PC, which delays its ignition and reduces, to some extent, the heat released during the combustion. To try to evidence such effect, TG analyses were performed under pyrolytic conditions on the raw materials and on the systems designed. Detailed data are gathered in Electronic Supplementary Information, Table S1 and Figure S1.

The silicone resin is the material which is the most thermally stable at high temperature compared to the substrate and to the epoxy resin located between the two materials. Indeed, epoxy decomposes almost entirely such that a residual mass of 8 wt.% is left at 800 °C (with a maximum degradation rate at 384 °C), and then degrades at a higher temperature (558 °C). PC is a char forming polymer and undergoes branching and eventual crosslinking to form an insoluble gel during its decomposition [45]. It releases carbon dioxide and bisphenol-A with lesser amounts of carbon monoxide, methane, phenol diphenyl carbonate, and 2(4-hydroxyphenyl)-2-phenyl propane during its degradation [46]. The epoxy resin also releases bisphenol A during its decomposition, as well as other phenolic products.

The decomposition of the silicone resin involves a three-step process and shows an excellent thermal stability (residual mass of 73 wt.% at 800 °C). The first degradation step corresponds to the release of silicone oligomers (3 wt.%) and the second and third steps (overlapped) correlate to the release of aromatic compounds (such as benzene and bisphenyl, 24 wt.%) [47]. The silicone resin is thermally more stable at high temperature (above 540 °C) compared to the polycarbonate, and also to the epoxy resin when the latter one is crosslinked. Under pyrolytic conditions, its main degradation step occurs at much higher temperature and with a lower degradation rate (0.2%/°C compared to 1.8 and 1.3%/°C respectively with the PC and the epoxy resin). Finally, its remaining mass at 800 °C is equivalent to three times the amount of residue for PC. The silicone resin is thus the material which is the most thermally stable at high temperature compared to the substrate and to the epoxy resin which composes the layer in between the two materials.

During a fire scenario, as it is located in the upper layer of the film, the silicone will be the first resin in contact with the open flame or exposed to the heat source. Consequently, a reasonable assumption is that the silicone resin brings the fire performances to the coated system
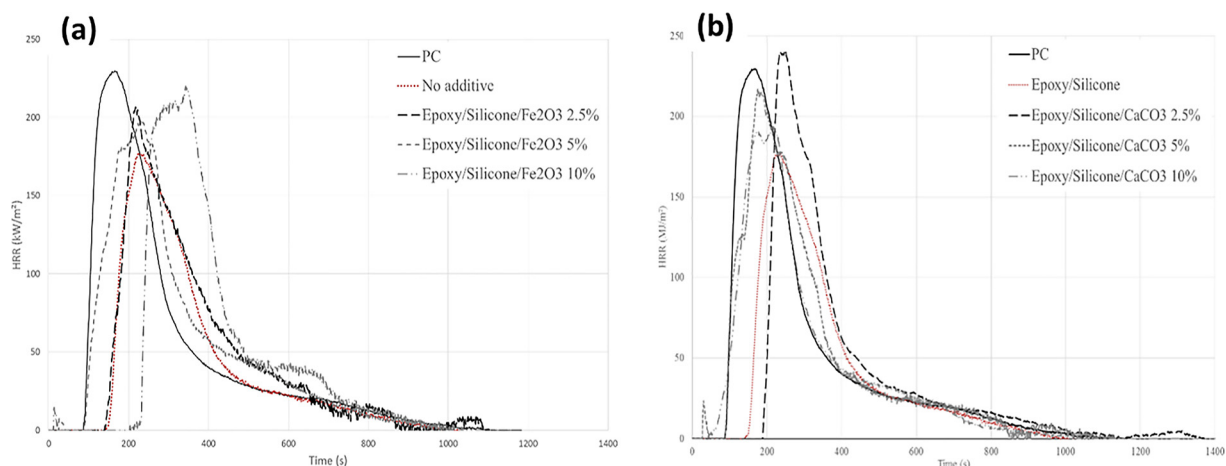
Fig. 4. HHR curves obtained for uncoated and coated PC with the epoxy/silicone/Fe$_2$O$_3$ system (a) and epoxy/silicone/CaCO$_3$ system at 50 kW/m^2.

in accordance with the thermal stability of the materials. The silicone coating may soften upon heating, and then expand to some extent to protect the underlying epoxy resin and substrate. From the previous experiments, it was observed that the presence of iron oxide and calcium carbonate limits the flame propagation along the sample and prevents the dripping, thus enhancing the fire retardant properties of PC. Charring seems also to be increased. In the literature, it is established that metal oxide particles promote the formation of a crosslinked network that may prevent the release of small molecules such as volatiles (thermal barrier effect). In particular, iron containing compounds may have a catalytic action, acting as synergists and smoke suppressants in some thermoplastic polymer formulations [48,49]. The use of $CaCO_3$ in silicone matrices has also been recently introduced: its use actually allows diluting the amount of fuel to be consumed. In addition, the mechanism was correlated with ceramization phenomena [50].

To try to evidence such effect, TG analyses were performed on the dried silicone film containing or not iron oxide (10 wt.% i.e. 2.5 vol.%) and calcium carbonate (2 wt.% i.e. 2.5 vol.%). Thermogravimetric derivatives were also calculated. Only the silicon resin was considered, as it is the resin directly exposed to the flame (Fig. 5). Detailed data are gathered in Electronic Supplementary Information, Table S2 (with iron oxide) and Table S3 (with calcium carbonate). This amount was chosen as it offers the most promising results in terms of fire retardant enhancements, visual appearance and adhesion.

The silicone film degrades in two steps while exhibiting an excellent thermal stability (residual weight of 68 wt.% at 800 °C). The first degradation step may be coupled with the release of the remaining solvents from the resin's preparation and the release of silicone oligomers (11 wt.%) [47]. The presence of Fe_2O_3 and $CaCO_3$ particles shifts the decomposition of the silicone resin toward higher temperatures. Additionally, with an initial loading of respectively 10 and 2 wt.%, the residue left is 72% and 70% compared to 68% without filler, approximately what was expected from the original inorganic addition in the case of Fe_2O_3 (-1 wt.%). With $CaCO_3$, the residual mass is slightly higher than expected ($+7\%$): the introduction of 2 wt.% of calcium carbonate favors the formation of additional carbonaceous char during burning.

In contrast, the formation of an expanded foamed structure is evidenced at 300 °C (Fig. 6a–c). A recent paper established that the increase in expansion of a coating results in an insulative barrier in the case of this particular silicone resin, which has a low thermal conductivity (0.18 W/m K) at 300 °C compared to the conductivity of PC (0.24 W/m K) [51]. The incorporation of iron oxide allows the formation of more widely spaced cells compared to the pure silicone resin. In addition, the presence of open cells (Fig. 6b) is evidenced compared to that of the neat resin (Fig. 6a). Although the formation of more widely spaced cells could be beneficial for the formation of a more efficient barrier, on the contrary, the presence of open cells could lead to the

opposite effect. In addition, the thermal conductivity of iron oxide is quite high compared to that of the silicone resin and PC (0.58 W/m K compared to 0.20 and 0.35 W/m K respectively for PC and for the silicone resin at 25 °C). Accordingly, the assumptions about the formation of a more insulative barrier cannot be evidenced. Finally, at 300 °C, no agglomeration of particles is detectable; nevertheless some areas appear lighter on the numerical pictures.

In the case of calcium carbonate (Fig. 6c), the structure exhibits smaller cells compared to the neat silicone. As it is established that the increase of the expansion of a coating could result in a thicker insulative barrier with the silicone [49], the improvements obtained during the fire tests could thus be the results of the formation of a cohesive thermal barrier at the surface of PC during combustion. In both cases, the dispersion of the particles seems still uniform at 300 °C although the silicone has started to degrade.

The thermogravimetric analyses allow highlighting the presence of specific interactions between polymer and additives depending on the temperature. It appears that the addition of iron oxide induces some thermal stabilization of the silicone resin in the range of temperature experimented (up to 5 wt.%/°C at 580 °C). This stabilization suggests that the filler somehow interacts with the silicone matrix, nevertheless not in a significant way according to the results. Similarly, the addition of calcium carbonate also induces a stabilization of the resin system (from about 5 wt.%/°C) up to 643 °C. Beyond this temperature, interactions become more stringent as the filler has started to degrade. Due to those specific interactions, the particles could act as a thermal barrier and retain product volatilization and thermal transport during the decomposition of PC. In the literature, it is shown that iron oxide nanoparticles could limit the thermal conduction inside the material, and at the same time decrease the kinetics of degradation of the resin [52,53]. In addition, mineral fillers are well known to release inert gases during the combustion process, leading to a cooling effect and to the formation of a protective layer at the surface of the polymer. This behavior could partially explain the nature of the interaction between the silicone and the fillers [35,54].

The higher thermal stability of both the silicone and the silicone/fillers systems compared to the substrate is in good agreement with the shift of TTI observed during MLC test: indeed, the silicone system is directly exposed to the radiative heat source (at 50 kW/m²) during the test and tends to protect the underlying epoxy and PC. As a consequence, a reasonable assumption would be that silicone improves the thermal stability of the system and thus creates a barrier to degradation gases between the heat source and the underlying substrate. This would also be in accordance with the behavior of the coated systems when exposed to a flame: the ignitability and combustibility of the material is slightly reduced thanks to the application of the film. Finally, preliminary thermogravimetric analyses demonstrated that the silicone resin, which is directly in contact with the heat source or with the flame, is thermally more stable than the substrate and the epoxy base-
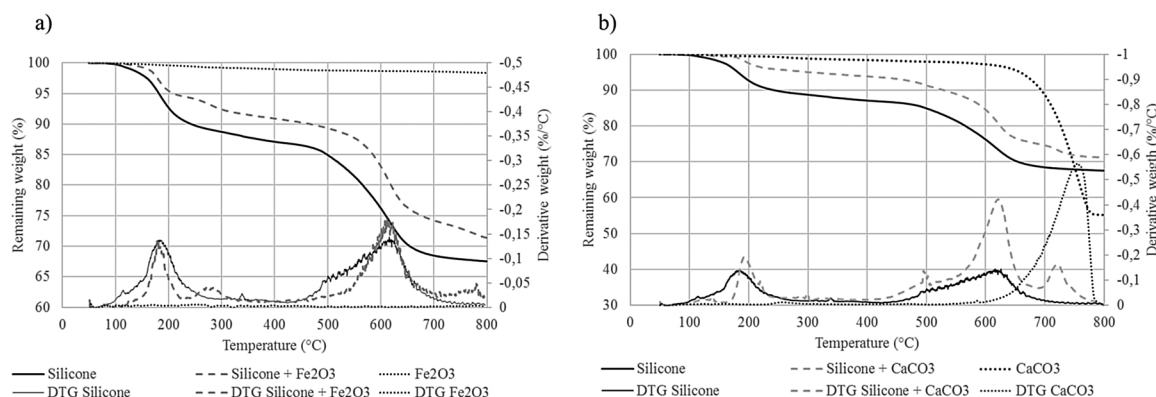

Fig. 5. Comparison of TG and DTG curves of the silicone systems with and without (a) Fe_2O_3 and (b) $CaCO_3$ at a heating rate of 20 °C min^{-1} under N_2.
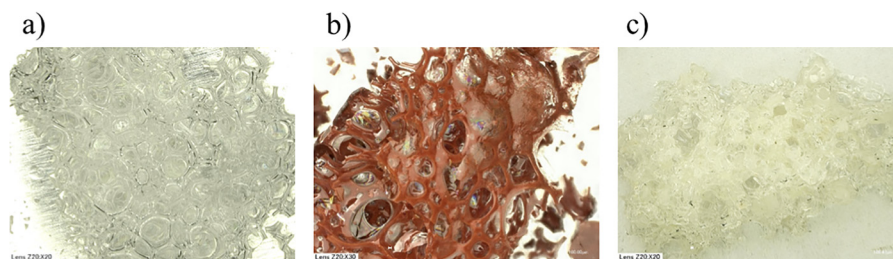
Fig. 6. Numerical picture of (a) silicone, (b) silicone/Fe_2O_3 and (c) silicone/$CaCO_3$ residue at 300 °C (Z20*20).
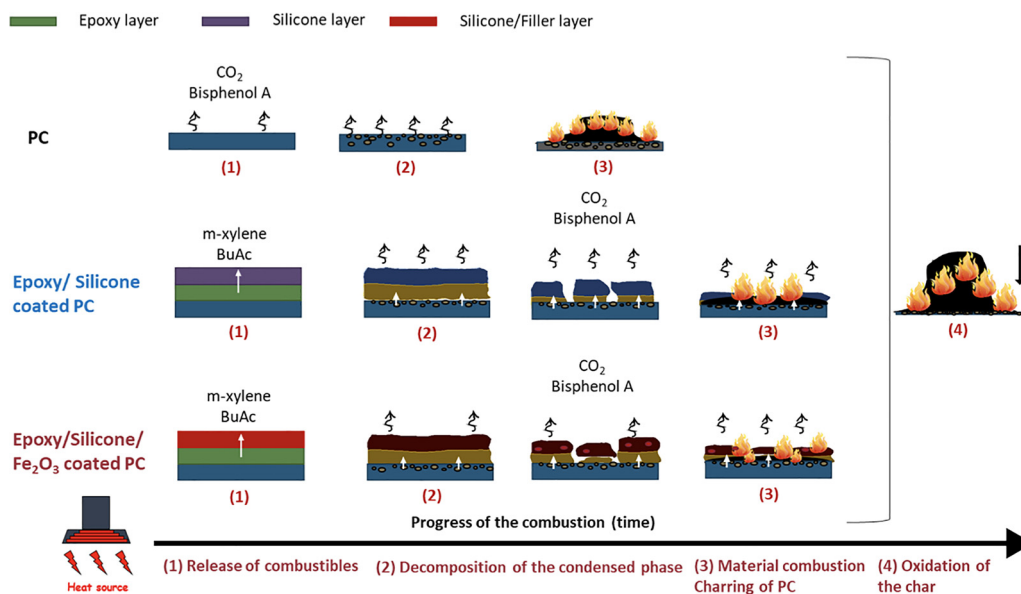

Fig. 7. Schematic representation of the mode of action of the PC coated with the epoxy/silicone and epoxy/silicone/iron oxide system.

coat layer, under inert conditions. In addition, the epoxy/silicone coating exhibits a significantly reduced rate of heat release compared to the epoxy resin considered separately. Accordingly, the formation of a barrier layer when the epoxy/silicone coating is applied on PC is noted, particularly at MLC test which evidenced a delay of the ignition time (+56 s).

The addition of whether iron oxide or calcium carbonate does not influence the thermal stability of the silicone polymer in a significant way under inert conditions. Contrary to our expectations, the presence of fillers when the coating is exposed to a radiative heat flux (MLC) does not lead to any significant change in the properties of the epoxy/silicone system: the behaviors of the epoxy/silicone/Fe_2O_3 and epoxy/silicone/$CaCO_3$ films are rather the same compared to the unfilled system, except for the TTI which is slightly increased in presence of fillers. At the opposite, in the presence of a flame, the enhancements are considerable: dripping is avoided; lower combustion time and flame spread are observed. A condensed phase mechanism may be supposed to contribute to the action of iron and carbonate particles. In addition, the incorporation of iron oxide does not promote the formation of additional residue, i.e. the formation of a char layer at the surface of PC. Nevertheless, it highly reduces the combustibility and ignitability of the silicone when submitted to a flame. This effect is also noticeable under a radiative heat source as the TTI is shifted (particularly when 10 wt.% is added to the system). Also, it is well known that the use of calcium carbonate particles in various systems can considerably increase the LOI value (for example in acrylate and EVA copolymer [50,55] and when combined to silicone elastomer [56,57]). The enhancement is mainly suggested to be due to the synergistic formation from silicone and calcium carbonate of a stable foam structure covered by chars that act as a heat barrier. This effect is confirmed by the foam structure

observed at 300 °C, the higher amount of residue obtained and the observation of the remaining specimens from LOI and UL-94 tests. Finally, the formation of this barrier layer at the surface of PC allows preventing the combustible gases from maintaining the flame [57] and thus it increases the fire performances of the system.

To conclude, the best improvements in terms of LOI are reached with the system containing the highest amount of fillers (10 vol.%). However, adhesion is slightly impacted (4B compared to 5B with a lower amount of fillers). 2.5 vol.% thus represents the best compromise: good fire performances are obtained, meanwhile the best adhesion rating is maintained. Vertical burning test shows significant enhancement in terms of fire performance compared to the unfilled system whereas mass loss results are similar (or even slightly worse) to the unfilled system at 50 kW/m².

Based on primary gas phase and condensed phase analysis [58], it is expected that the presence of either iron oxide and calcium carbonate modifies the silicone network, resulting in a modification of the ratio of the competitive reaction occurring when the silicone degrades (evolution of silicone fragment vs. crosslinking). Finally, it can also be proposed that the presence of fillers improves the protective properties of the barrier layer between the heat source or the flame and the underlying materials (the base layer and the substrate). With calcium carbonate, charring phenomenon is also evidenced. Two hypotheses can thus be drawn: either the mechanical properties of this layer, mostly mineral, are reinforced by the presence the particles or the presence of iron oxide and calcium carbonate modifies the structure of the silicon network. Raman spectroscopy presented earlier in the paper (Fig. 2) tends to confirm this last hypothesis.

In order to sum up the results obtained, a schematic representation of the mode of action of the coated PCs compared to the raw PC when

submitted to a radiative heat source, i.e. MLC test, under a flux of 50 kW/m² (794 °C) is proposed (Fig. 7).

3.3. Impact of aging on the coated polycarbonate

Aging tests (T/UV and T/RH) were performed on virgin PC, and on PC coated with the epoxy/silicone and epoxy/silicone/Fe₂O₃ systems, as silicone is well known to be hydrophobic and iron oxide is also well known to have good aging properties due to its capacity to absorb UV A compared to calcium carbonate [22,59].

3.3.1. Virgin polycarbonate

The yellowing and the decrease in physical properties of PC over aging has been a scientific subject for a very long time. It has been widely acknowledged that degradation mechanisms of polycarbonate depend on the irradiation wavelengths: (i) below 300 nm, the yellowing is due to the photo-Fries rearrangement (insignificant during outdoor exposure since solar radiations are longer than 300 nm); and (ii) at longer wavelengths (310–350 nm), impurities and defects in the polymer chain are responsible for the yellowing [60–63]. As supposed, the PC plates become yellow when exposed to UV rays (340 nm: b^* varies from −3.9 to 11.9 after 8 weeks under UV) whereas they remain unchanged under T/RH conditions. Nevertheless, no defects appear on the surface of the plate both under UV and T/RH conditions (Fig. 8, Table 5).

Fire performances remain constant after 2 weeks of exposure to both weathering conditions at UL-94 and LOI (Table 5). However, they start to decrease after 4 weeks of exposure: a loss of 1 vol.% in the LOI value is obtained every two weeks. Considering the UL-94 test, PC remains NC. However, a difference in the flaming time of around 10 s is observed between UV and R/TH aged samples (UV aged samples being the worst, see ESI Table S4). The difference in burning time between the non-aged and T/RH aged samples remains lower than 10 s for all aging durations, and lower than 20 seconds between the non-aged and UV aged samples. The higher degradation rate of PC considering UV aging is also observed with the LOI values: 25 vol.% is registered after 8

weeks of exposure under UV conditions versus 26 vol.% under T/RH. Virgin PC is thus more affected by UV aging compared to T/RH conditions.

Finally, a slight reduction of the pHRR is observed for the aged samples at MLC (Table 6). Nevertheless the values remain close to the range of the experimental error of the apparatus (respectively −15 and −13% after UV and T/RH aging).

3.3.2. Polycarbonate coated with epoxy/silicone self-stratified coating
3.3.2.1. Under UV. Results show an evolution in color of the plates coated with the epoxy/silicone blend during aging under UV (Table 7). Indeed, ΔE^* between the unaged and aged samples reaches 25.9 after 8 weeks of exposure. L^* is constant and a^* varies from −0.4 to −2.7. It means that there is a slight color change which tends toward green after aging. Finally, the major change is registered with the b^* value. It increases from −3.9 to 21.8 after 8 weeks of aging: the color of the coated samples tends to yellow over aging.

The comparison with the data of raw PC shows that yellowing appears faster (from the first two weeks of aging) and is even more pronounced when a coating is applied. This yellowing could be reasonably attributed to the epoxy resin, which is well known for having poor resistance to UV [64]. Indeed, few hours under UV exposure lead to the chalking and yellowing of the epoxy resin due to photo-degradation (similar to that of PC). Moreover, neither blistering nor removal of paint is noticed during the test: the best rating (5B) is still obtained after 8 weeks of weathering. No change in the fire retardant properties at LOI and UL-94 tests compared to the non-aged samples is observed, whatever the weathering conditions. Nevertheless, a shift of the TTI toward lower values is observed at MLC test after 8 weeks of aging, and pHRR slightly increases (Table 8): the change of the properties of the epoxy may be responsible for this shift and affects somehow the silicone resin. Indeed, it is well known that silicones are highly stable under UV rays in the 300–400 nm range [65].

3.3.2.2. Under T/RH. Visually, no change in color is detectable on aged samples, even after 8 weeks of aging (Fig. 8). $L^*a^*b^*$ measurements confirm this observation: ΔE^* is negligeable ($\Delta E^* < 3.6$ for all aged samples). Moreover, neither blistering nor change in visual appearance is registered. Adhesion properties are also maintained, as well as LOI values and UL-94 rating (Table 8). However, at the MLC test, ignition of the epoxy/silicone coated PC after 8 weeks of aging occurs much earlier compared to the non-aged sample. In addition, both THR and pHRR are increased. Aging of silicone resins under humidity conditions have already demonstrated some changes in the properties, mainly resulting from the decomposition of the chemical bonding between polysiloxane backbones and methyl groups. This hydrolysis leads to the formation of polar siloxanols, which can also condense to rigid crosslinked structures [66,67]. In addition, it turned out that water molecules from humidified gases can accelerate aging, leading to a loss of properties [68].

3.3.3. Polycarbonate coated with epoxy/silicone/Fe₂O₃ self-stratified coating
Both under UV and T/RH conditions, no change in the visual appearance ($\Delta E^* < 3.7$) and in the adhesion (5B rating is kept for all samples) are noticeable (Table 7): the coating prevents UV rays from reaching the substrate. Lastly, no modification of the fire behavior is observed over aging: the excellent fire properties are influenced neither by UV rays, temperature nor by humidity (Table 8).

To conclude on aging studies, T/RH weathering tests are very conclusive for coated samples: slight change is registered after 8 weeks of exposure which do not significantly modify the ability of the coating to prevent from the decrease of the fire performances of PC itself. Neither modification in the adhesion nor in the quality of the films is observed both under T/RH and UV exposure. Under UV, the coating also allows preserving the adhesion and fire properties of the
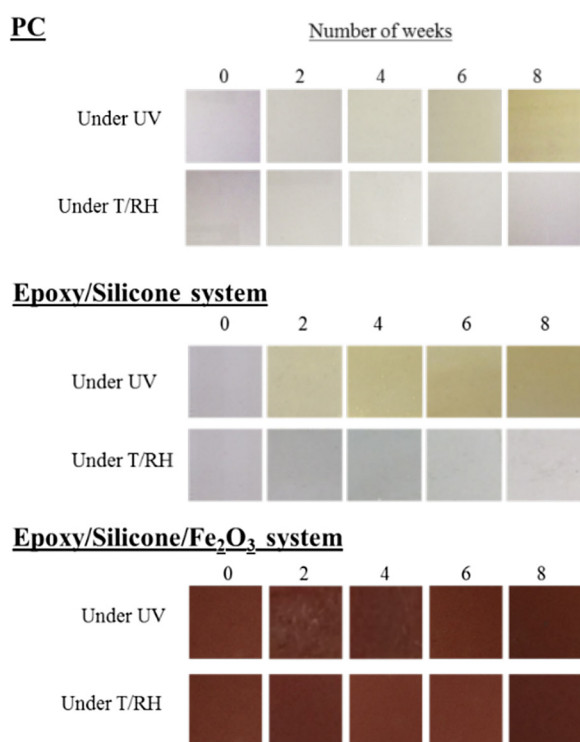
Fig. 8. Visual appearance of the PC and coated PC after UV and T/RH exposure.

Table 5
L*a*b*, UL-94 and LOI values determined after weathering tests of polycarbonate under UV and T/RH conditions.

Time (week)	Before aging	Under UV				Under T/RH			
	0	2	4	6	8	2	4	6	8
L*	87.5	87.4	87.7	85.0	87.8	87.3	87.8	87.6	87.8
a*	−0.8	−0.7	−1.4	−2.2	−2.7	−0.0	−0.1	−0.1	−0.1
b*	−3.9	−1.3	2.2	8.1	11.9	−3.8	−4.0	−3.8	−3.9
ΔE*	–	1.6	5.1	11.3	15.1	1.3	1.4	1.2	1.4
UL-94	NC	NC				NC			
LOI (vol.%)	28	28	27	26	25	28	27	26	26

Table 6
MLC data of the virgin PC before aging, and after 8 weeks of aging under UV and T/RH conditions.

Polycarbonate			
Aging (8 weeks)	No aging	UV	T/RH
TTI (s)	92	90	83
TFO (s)	1077	915	936
pHRR (kW/m²)	231	197 (−15%)	202 (−13%)
THR (MJ/m²)	52	53 (+2%)	46 (−12%)

specimens. However, the unfilled coating does not prevent from the infiltration of UV rays which are responsible for the yellowing of the substrate. In this case, the epoxy resin also yellows under UV rays leading to an increase of the yellowing for the whole system. On the contrary, no yellowing is registered for PC coated with the filled epoxy/silicone system.

4. Conclusion

One pot fire retardant self-layered coatings based on epoxy/silicone blends have been fully characterized and a better understanding of the influence of two fillers (iron oxide and calcium carbonate) on the self-stratifying process when incorporated from 2.5 to 10 vol.% was provided. Flame retardant properties of the successful coatings have been evaluated, as well as the effect of aging over 8 weeks when iron oxide is

added to the system. Finally, an understanding of the mode of action of the coating to protect the polycarbonate was proposed.

Self-stratified coatings based on a combination of epoxy, silicone resins and fillers were designed: the topcoat layer was found to be composed of the silicone resin, and the base layer of the crosslinked epoxy resin, whatever the additive incorporated in the system. Microscopic analyses have demonstrated that fillers do not impact the stratification process. However their migration to the upper layer of the coating (silicone phase) was not always optimal. Particularly, the wetting of calcium carbonate by the epoxy medium when introduced at 10 vol.% was found to be complex.

On the one hand, the efficiency of the coatings to fire protect the PC matrix has been tested under two fire scenarios, i.e. under a radiative heat source or a flame, using MLC, UL-94 and LOI fire tests. From those results, the best improvements in terms of LOI are obtained with the system containing the highest amount of fillers (10 vol.%). However, adhesion of the coating is slightly impacted (4B compared to 5B with the unfilled system). 2.5 vol.% thus represents the best compromise: good fire performances are obtained at LOI and UL-94 tests meanwhile the best adhesion rating is maintained. Vertical burning test shows significant enhancement in terms of fire performances compared to the unfilled system (no dripping, short combustion time and flame spread) whereas mass loss results are similar (or even slightly worse) in terms of heat release compared to the unfilled system at 50 kW/m². Indeed, the reduction of the heat released during combustion is mainly due to the epoxy/silicone system. Nevertheless, the addition of fillers allows a significant delay of the ignition time of the systems. The best

Table 7
L*a*b*, adhesion, UL-94 and LOI values determined after weathering tests of coated PC under UV and T/RH conditions.

Coated PC with epoxy/silicone system									
Time (week)	Before aging	Under UV				Under T/RH			
	0	2	4	6	8	2	4	6	8
L*	85.6	85.9	85.8	86.3	84.4	89.2	88.3	88.6	88.4
a*	−0.4	−2.0	−2.4	−2.4	−2.7	−0.1	−0.0	−0.2	−0.1
b*	−3.9	13.5	14.7	14.4	21.8	−4.5	−3.7	−3.5	−3.4
ΔE*	–	17.5	18.7	18.4	25.9	3.6	2.7	3.0	2.8
Adhesion	5B	5B				5B			
UL-94	V0	V0				V0			
LOI (vol.%)	28	28				28			

Coated PC with epoxy/silicone/Fe₂O₃ system									
Time (week)	Before aging	Under UV				Under T/RH			
	0	2	4	6	8	2	4	6	8
L*	36.5	38.3	36.3	32.8	35.2	36.1	35.8	35.7	36.1
a*	19.1	17.5	19.0	19.3	17.1	18.5	18.8	19.9	19.0
b*	11.7	11.5	12.2	12.3	12.1	11.7	11.5	12.2	11.6
ΔE*	–	2.4	0.5	3.7	2.3	0.7	0.8	1.2	0.4
Adhesion	5B	5B				5B			
UL-94	V0	V0				V0			
LOI (vol.%)	33	33				33			

Table 8
MLC data of the PC coated respectively with the epoxy/silicone and epoxy/silicone/Fe_2O_3 formulations before aging, and after 8 weeks of aging under UV and T/RH conditions.

Aging (8 weeks)	Epoxy/Silicone coated PC			Epoxy/Silicone/Fe_2O_3 coated PC		
	No aging	UV	T/RH	No aging	UV	T/RH
TTI (s)	148 ± 7	98	72	141 ± 20	127	110
TFO (s)	903 ± 6	689	852	1003 ± 33	1034	934
pHRR (kW/m^2)	176 ± 4	189 (+7%)	212 (+20%)	205 ± 20	181 (−12%)	200 (−2%)
THR (MJ/m^2)	41 ± 3	41 (+0%)	61 (+50%)	47 ± 2	50 (+6%)	51 (+9%)

improvements in terms of pHRR and THR are obtained with the system containing 10 vol.% of fillers, but at the expense of the TTI which is shortened.

On the other hand, the formation of an efficient barrier layer in presence of the particles was found to be the main mode of action of the fillers: mass transfers were especially decreased, thus limiting the feeding of the flame. The detailed mode of action has not been ascertained and a number of hypotheses may be considered, a beneficial effect on the silica residue morphology being our most likely explanation.

Finally, a great resistance over aging under T/RH is obtained when both the unfilled and filled coatings containing iron oxide are applied on PC. Under UV, the yellowing of the unfilled coating and of the polycarbonate is accelerated whereas the filled coating completely protects the underneath substrate from UV rays attack. Additionally, both the unfilled and filled silicone-based coatings prevent from the decrease of the fireproofing performances registered in the presence of a flame after the aging of the raw PC. The only issues encountered with the epoxy/silicone coating were solved by the incorporation of iron oxide particles.

This work is the first study highlighting the potential of self-stratifying compositions to produce fire retardant coatings. The potential of such coating is very wide and can be applied for a variety of coatings composition. This work confirms that self-stratifying fire retardant coatings may be valorized as flame retardant surface treatments for polymeric substrates and offers the possibility of developing more sustainable and efficient coatings.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.porgcoat.2019.105269.

References

[1] M. Jimenez, S. Duquesne, S. Bourbigot, Fire protection of polypropylene and polycarbonate by intumescent coatings, Polym. Adv. Technol. 23 (2012) 130–135.
[2] S. Duquesne, M. Jimenez, S. Bourbigot, 11th FRPM'07 on Fire Retardancy of Polymers: New Strategies and Mechanisms, Bolton, UK, 2009, pp. 240–252.
[3] C. Pagella, R. Epifani, Intumescent coatings for polymer substrates, PPCJ Polym. Paint Colour J. 203 (2013) 38–41.
[4] S. Duquesne, M. Jimenez, S. Bourbigot, Aging of the flame-retardant properties of polycarbonate and polypropylene protected by an intumescent coating, J. Appl. Polym. Sci. 131 (2014) 39566.
[5] R. Berkau, M. Gailberger, T. Gruber, K. Holdik, G. Meichsner, F. Mezger, Coating composition for forming self-layering or self-coating lacquer systems, US7186772, filled by Daimler Chrysler A.G., in: U.S. Patent (Ed.), 2007.
[6] V.V. Verkholantsev, Nonhomogeneous-in-layer coatings, Prog. Org. Coat. 13 (1985) 71–96.
[7] E. Langer, H. Kuczyńska, E. Kamińska-Tarnawska, J. Łukaszczyk, Self-stratifying coatings containing barrier and active anticorrosive pigments, Prog. Org. Coat. 71 (2011) 162–166.
[8] A. Beaugendre, S. Degoutin, S. Bellayer, C. Pierlot, S. Duquesne, M. Casetta, M. Jimenez, Self-stratification of ternary systems including a flame retardant liquid additive, Coatings 8 (2018) 448.
[9] A. Beaugendre, S. Saidi, S. Degoutin, S. Bellayer, C. Pierlot, S. Duquesne, M. Casetta, M. Jimenez, One pot flame retardant and weathering resistant coatings for plastics: a novel approach, RSC Adv. 7 (2017) 40682–40694.
[10] S. Benjamin, C. Carr, D.J. Walbridge, Self-stratifying coatings for metallic substrates, Prog. Org. Coat. 28 (1996) 197–207.
[11] A. Toussaint, Self-stratifying coatings for plastic substrates (brite euram project RI 1B 0246 C(H)), Prog. Org. Coat. 28 (1996) 183–195.
[12] J. Baghdachi, H.R.P. Hernandez, C.G. Templeman, Self-stratifying automotive topcoat compositions and processes, US 2010/0087596 A1, filled by Toyota Motor Engineering & Manufacturing North America, in: U.S. Patent (Ed.), 2010.
[13] L. Wu, J. Baghdachi, Self-stratifying polymers and coatings, in: L. Wu, J. Baghdachi (Eds.), Functional Polymer Coatings – Principle, Methods and Applications, John Wiley & Sons, Inc, Hoboken, NJ, USA, 2015, pp. 197–217.
[14] A. Beaugendre, S. Degoutin, S. Bellayer, C. Pierlot, S. Duquesne, M. Casetta, M. Jimenez, Self-stratifying epoxy/silicone coatings, Prog. Org. Coat. 103 (2017) 101–110.
[15] V.V. Verkholantsev, M. Flavian, Polymer structure and properties of heterophase and self-stratifying coatings, Prog. Org. Coat. 29 (1996) 239–246.
[16] P. Vink, T.L. Bots, Formulation parameters influencing self-stratification of coatings, Prog. Org. Coat. 28 (1996) 173–181.
[17] P. Carty, E. Metcalfe, S. White, A review of the role of iron containing compounds in char forming/smoke suppressing reactions during the thermal decomposition of semi-rigid poly(vinyl chloride) formulations, Polymer 33 (1992) 2704–2708.
[18] G.A. Olah, Friedel Crafts and Related Reactions vol. 1, General Aspects, Interscience Publishers, A Division of John Wiley & Sons, New York, NY, 1963.
[19] H. Marsh, D. Crawford, D.W. Taylor, Catalytic graphitization by iron of isotropic carbon from polyfurfuryl alcohol, 725–1090 K. A high resolution electron microscope study, Carbon 21 (1983) 81–87.
[20] C.D. Hurd, W.H. Tallyn, Optimum conditions for the preparation of ketene from acetone, J. Am. Chem. Soc. 47 (1925) 1427–1430.
[21] P. Carty, B.M. Adger, Iron-containing organometallic compounds as flame-retarding/smoke-suppressing additives for semi-rigid poly(vinyl chloride), Appl. Organ. Chem. 4 (1990) 127–131.
[22] L. Truffault, Synthèse et caractérisation de nanoparticules à base d'oxydes de cérium et de fer pour la filtration des UV dans les produits solaires (PhD thesis), Université d'Orléans, 2010.
[23] W.P. Whelan, Synergistic flame-retardant activity of iron compounds in halogen-containing nitrile polymer compositions, J. Fire Retard. Chem. 6 (1979) 206–219.
[24] P. Carty, E. Metcalfe, T.J. Saben, Thermal analysis of plasticized PVC containing flame retardant/smoke suppressant inorganic and organometallic iron compounds, Fire Saf. J. 17 (1991) 45–56.
[25] A. Laachachi, M. Cochez, M. Ferriol, J.M. Lopez-Cuesta, E. Leroy, Influence of TiO_2 and Fe_2O_3 fillers on the thermal properties of poly(methyl methacrylate) (PMMA), Mater. Lett. 59 (2005) 36–39.
[26] R.L. Markezich, Flame retardants: synergisms involving halogens, in: G. Pritchard (Ed.), Plastics Additives: An A–Z Reference, Springer Netherlands, Dordrecht, 1998, pp. 327–338.
[27] E.D. Weil, N.G. Patel, Iron compounds in non-halogen flame-retardant polyamide systems, Polym. Degrad. Stabil. 82 (2003) 291–296.
[28] M.M. Hirschler, Reduction of smoke formation from and flammability of thermoplastic polymers by metal oxides, Polymer 25 (1984) 405–411.
[29] K.J. Nangrani, R. Wenger, P.G. Daugherty, Effect of pigments on the flammability of reinforced thermoplastics, Plast. Comp. 11 (1988) 27–31.
[30] N.A. Isitman, M. Dogan, E. Bayramli, C. Kaynak, Fire retardant properties of intumescent polypropylene composites filled with calcium carbonate, Polym. Eng. Sci. 51 (2011) 875–883.
[31] S. Bellayer, E. Tavard, S. Duquesne, A. Piechaczyk, S. Bourbigot, Mechanism of intumescence of a polyethylene/calcium carbonate/stearic acid system, Polym. Degrad. Stab. 94 (2009) 797–803.
[32] F. Laoutid, M. Lorgouilloux, D. Lesueur, L. Bonnaud, P. Dubois, Calcium-based

hydrated minerals: promising halogen-free flame retardant and fire resistant additives for polyethylene and ethylene vinyl acetate copolymers, Polym. Degrad. Stab. 98 (2013) 1617–1625.

[33] S. Hamdani-Devarennes, C. Longuet, R. Sonnier, F. Ganachaud, J.-M. Lopez-Cuesta, Calcium and aluminum-based fillers as flame-retardant additives in silicone matrices. III. Investigations on fire reaction, Polym. Degrad. Stab. 98 (2013) 2021–2032.

[34] L. Karlsson, A. Lundgren, J. Jungqvist, T. Hjertberg, Influence of melt behaviour on the flame retardant properties of ethylene copolymers modified with calcium carbonate and silicone elastomer, Polym. Degrad. Stab. 94 (2009) 527–532.

[35] S. Fallis, R. Reed, Y. Lu, Advanced propellant/additive development for fire suppressing gas generators, Halon Options Technical Working Conference (2000) 361.

[36] A. Ram, O. ZIlber, S. Kenig, Polym. Eng. Sci. 25 (9) (1985) 535–540.

[37] ISO-4892-3, Methods of Exposure to Laboratory Sources – Part 3: Fluorescent UV Lamps, (2013).

[38] V. Resta, G. Quarta, M. Lomascolo, L. Maruccio, L. Calcagnile, Raman and photoluminescence spectroscopy of polycarbonate matrices irradiated with different energy 28Si+ ions, Vacuum 116 (2015) 82–89.

[39] H.G.M. Edwards, S.E.J. Villar, J. Jehlicka, T. Munshi, FT-Raman spectroscopic study of calcium-rich and magnesium-rich carbonate minerals, Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 61 (2005) 2273–2280.

[40] B. Ahmmad, K. Leonard, M. Shariful Islam, J. Kurawaki, M. Muruganandham, T. Ohkubo, Y. Kuroda, Green synthesis of mesoporous hematite (α-Fe₂O₃) nanoparticles and their photocatalytic activity, Adv. Powder Technol. 24 (2013) 160–167.

[41] A.M. Abdel-Wahab, A.S. Al-Shirbini, O. Mohamed, O. Nasr, Photocatalytic degradation of paracetamol over magnetic flower-like TiO₂/Fe₂O₃ core-shell nanostructures, J. Photochem. Photobiol. A: Chem. 347 (2017) 186–198.

[42] K.V.A. Kumar, L. Chandana, P. Ghosal, C. Subrahmanyam, Simultaneous photocatalytic degradation of p-cresol and Cr (VI) by metal oxides supported reduced graphene oxide, Mol. Catal. 451 (2018) 87–95.

[43] T.C. Peck, G.K. Reddy, M. Jones, C.A. Roberts, Monolayer detection of supported Fe and Co oxides on ceria to establish structure-activity relationships for reduction of NO by CO, J. Phys. Chem. C 121 (2017) 8435–8443.

[44] S. Bourbigot, B. Gardelle, M. Jimenez, S. Duquesne, V. Rerat, Silicone-based coatings for reaction and resistance to fire of polymeric materials, 22nd Annual Conference on Recent Advances in Flame Retardancy of Polymeric Materials 2011 (2011) 243–251.

[45] Robertson, Thermal Degradation Studies of Polycarbonate, Virginia Polytechnic Institute, Blackburg, Virginia, 2001.

[46] H. Yan, C.-X. Lu, D.-Q. Jing, X.-l. Hou, Chemical degradation of amine-cured DGEBA epoxy resin in supercritical 1-propanol for recycling carbon fiber from composites, Chinese J. Polym. Sci. 32 (2014) 1550–1563.

[47] B. Gardelle, S. Duquesne, C. Vu, S. Bourbigot, Thermal degradation and fire performance of polysilazane-based coatings, Thermochim. Acta 519 (2011) 28–37.

[48] E. Gallo, U. Braun, B. Schartel, P. Russo, D. Acierno, Halogen-free flame retarded poly(butylene terephthalate) (PBT) using metal oxides/PBT nanocomposites in combination with aluminium phosphinate, Polym. Degrad. Stab. 94 (2009) 1245–1253.

[49] P. Carty, S. White, The importance of char forming reactions in thermoplastic polymers, Fire Mater. 18 (1994) 151–166.

[50] S.K. Srivastava, T. Kuila, Fire retardancy of elastomers and elastomer nanocomposites, Polymer Green Flame Retardants, Elsevier, Amsterdam, 2014, pp. 597–651 (Chapter 18).

[51] J.E.J. Staggs, Thermal conductivity estimates of intumescent chars by direct numerical simulation, Fire Saf. J. 45 (2010) 228–237.

[52] A. Laachachi, E. Leroy, M. Cochez, M. Ferriol, J.M. Lopez Cuesta, Use of oxide nanoparticles and organoclays to improve thermal stability and fire retardancy of poly(methyl methacrylate), Polym. Degrad. Stab. 89 (2005) 344–352.

[53] T. Kashiwagi, J.W. Gilman, K.M. Butler, R.H. Harris, J.R. Shields, A. Asano, Flame retardant mechanism of silica gel/silica, Fire Mater. 24 (2000) 277–289.

[54] T.R. Hull, A. Witkowski, L. Hollingbery, Fire retardant action of mineral fillers, Polym. Degrad. Stab. 96 (2011) 1462–1469.

[55] U. Andreasson, T. Uematsu, B.A. Sultan, M. Anker, O. Prieto, Flame retardant polymer composition, EP0393959B1, filled in by Borealis A.S, E.P. Office (Ed.), 2016.

[56] R.H. Krämer, P. Blomqvist, P.V. Hees, U.W. Gedde, On the intumescence of ethylene-acrylate copolymers blended with chalk and silicone, Polym. Degrad. Stab. 92 (2007) 1899–1910.

[57] A. Hermansson, T. Hjertberg, B. Sultan, Linking the flame-retardant mechanisms of an ethylene-acrylate copolymer, chalk and silicone elastomer system with its intumescent behaviour, Fire Mater. 29 (2005) 407–423.

[58] A. Beaugendre, Self-stratifying Flame Retardant Coatings for Plastics (PhD thesis), Université de Lille, France, 2017.

[59] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, Z.F. Liu, Use of iron oxide nanomaterials in wastewater treatment: a review, Sci. Total Environ. 424 (2012) 1–10.

[60] A.L. S.N.D. Andrady, L.F.E. Crewdson, Wavelength sensitivity of unstabilized and UV stabilized polycarbonate to solar simulated radiation, Polym. Degrad. Stab. 35 (1992) 237–247.

[61] M. Diepens, P. Gijsman, Influence of light intensity on the photodegradation of bisphenol A polycarbonate, Polym. Degrad. Stab. 94 (2009) 34–38.

[62] C.E. SH Hoyle, G.L. Nelson, Photochemistry of bisphenol-A based polycarbonate: the effect of the matrix and early detection of photoFries product formation, J. Polym. Sci. Part A: Polym. Chem. 30 (1992) 1525–1533.

[63] N. O.H. Nagai, T. Imai, I. Nishiyama, Depth profile analysis of the photochemical degradation of polycarbonate by infrared spectroscopy, Polym. Degrad. Stab. 81 (2003) 491–496.

[64] N. Rajagopalan, A.S. Khanna, Effect of nano-ZnO in lowering yellowing of aliphatic amine-cured DGEBA-based epoxy coatings on UV exposure, Int. J. Scient. Res. Publ. 3 (2013).

[65] C. Madeleine-Perdrillat, Approche expérimentale et théorique de la dégradation des polydiméthylsiloxanes (PhD thesis), Université Blaise Pascal, Clermont Ferrand, France, 2011.

[66] G. Ducom, B. Laubie, A. Ohannessian, C. Chottier, P. Germain, V. Chatain, Hydrolysis of polydimethylsiloxane fluids in controlled aqueous solutions, Water Sci. Technol. 68 (2013) 813–820.

[67] E.P. Plueddemann, Silane Couplings Agents, 2nde ed., Springer Science + Business Media, LLC, Midland, MI, USA, 1991.

[68] H. Chang, Z. Wan, X. Chen, J. Wan, J. Luo, H. Zhang, S. Shu, Z. Tu, Temperature and humidity effect on aging of silicone rubbers as sealing materials for proton exchange membrane fuel cell applications, Appl. Therm. Eng. 104 (2016) 472–478.