Electronic Supplementary Information

One pot flame retardant and weathering resistant coatings for plastics: a novel approach

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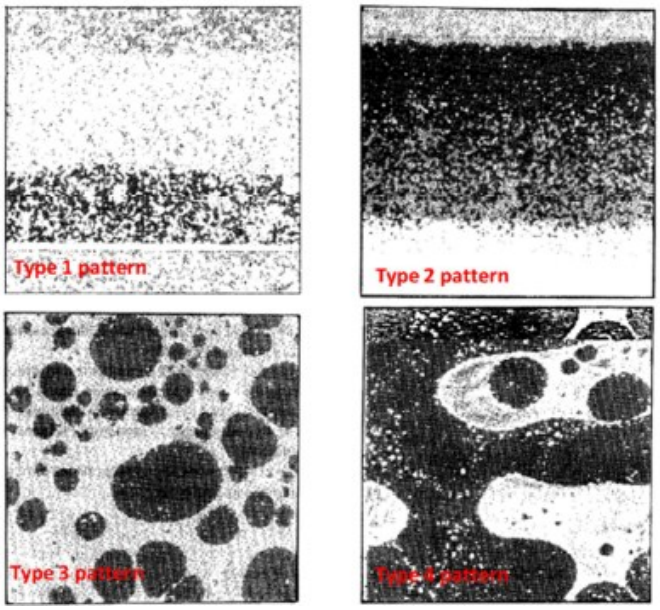

Figure S1. Classification of self-stratified coatings [Toussaint, A., Progress in Organic Coatings. 1996,**28**, 183-195]

Table S1. Values of the contact angle and surface tensions following Wu method of PC and resins [Wu, S. Polar and Nonpolar Interactions in Adhesion. Journal of Adhesion, 1973,**5**, 39-55.]

Substrate		θ_{water}(°)	$\theta_{diidomethane}$(°)	γ(mN.m^{-1})	γ^p(mN.m^{-1})	γ^d(mN.m^{-1})
Polycarbonate (Lexan)		77 ± 3	24 ± 2	55.4	8.9	46.6
Solvent	**Resins**	θ_{water} (°)	$\theta_{diidomethane}$(°)	γ(mN.m^{-1})	γ^p(mN.m^{-1})	γ^d(mN.m^{-1})
Xylene	Epoxy	104 ± 2	36 ± 3	37.0	-0.5	37.6
	Fluoropolymer	87 ± 1	50 ± 2	41.7	6.5	35.2
BuAc: xylene (50: 50)	Epoxy	87 ± 3	46 ± 4	43.3	6.2	37.1
	Fluoropolymer	84 ± 2	49 ± 3	43.6	7.6	36.0
MIBK: xylene (50: 50)	Epoxy	108 ± 7	36 ± 2	27.6	-1.8	29.4
	Fluoropolymer	80 ± 2	49 ± 1	45.4	9.3	36.0
MIBK: xylene: 1-methoxy-2-propanol (50: 30: 20)	Epoxy	74 ± 2	44 ± 3	49.8	11.5	38.3
	Fluoropolymer	78 ± 2	48 ± 2	46.3	9.7	36.5

Attenuated Total Reflexion (ATR) with a diamond crystal was used in conjunction with Fourier Transform Infrared spectroscopy (FTIR) to examine the materials and the top layer of the epoxy/fluoropolymer film. Resins were diluted following the procedure of preparation of the coating (diluted at 30 wt. % in a blend of BuAc: xylene (1:1), let dry for 24 hours at ambient temperature and cured for 2 hours at 110°C). The amine hardener was added to the epoxy resin to allow its curing. Room temperature FTIR-ATR spectra were recorded between 400 and 4000 cm^{-1} using a Fourier transform infrared spectrometer (ThermoScientific) Nicolet iS50. The spectra processed by OMNIC software resulted from 64 scans using a resolution of 4 cm^{-1}.

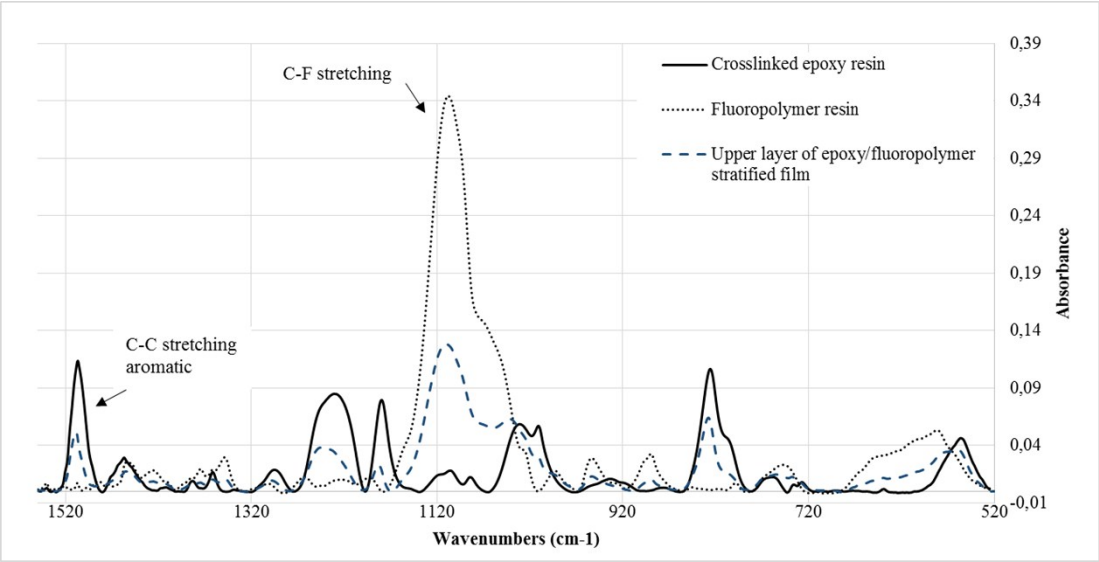

Figure S2FTIR spectra of the crosslinked epoxy and fluoropolymer resins, and of the top layer of the epoxy/fluoropolymer stratified film

Table S2. Contact angle and surface energy data of the crosslinked epoxy and fluoropolymer resins (no solvent)

	θ_{water}(°)	$\theta_{diodomethane}$(°)	γ	γ^d	γ^p
Fluoropolymer resin (100%)	**101 ± 2**	**63 ± 5**	**31**	**29**	**2**
Fluoropolymer resin ((30 wt.% in BuAc:xylene)	83 ± 2	49 ± 3	44	36	8
Crosslinked epoxy resin (100%)	**83 ± 11**	**96 ± 6**	**45**	**37**	**8**
Crosslinked epoxy resin (30 wt.% in BuAc:xylene)	87 ± 3	46 ± 4	43	37	6
Upper layer of the epoxy/fluoropolymer dry film	85 ± 2	55 ± 1	40	33	8

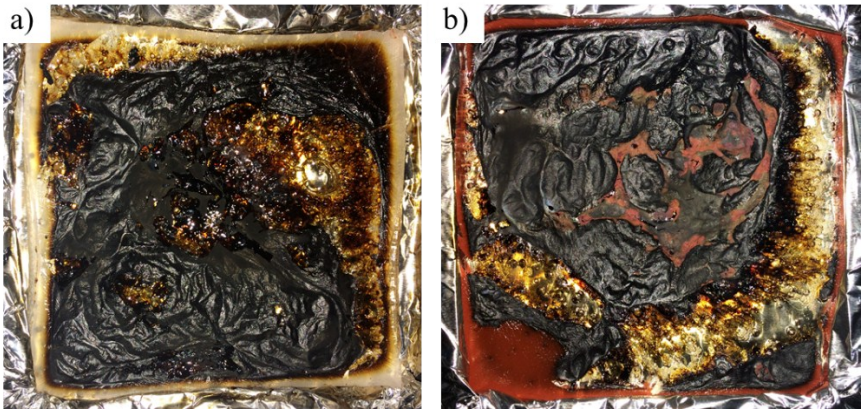

Figure S3. Samples of coated PC based on epoxy/fluoropolymer flamed out after ignition at the MLC test: a) without Fe_2O_3, b) with Fe_2O_3 particles

Thermogravimetric analyses (TGA) were carried out using a Discovery TGA provided by TA Instrument. Dry grounded coatings samples (10 mg) were put in alumina crucibles, and the tests

were performed after the samples followed the same experimental procedure as the coating (i.e dried for 24 hours at ambient temperature and cured for 2 hours at 110 °C). The nitrogen or air flow rate for all TG tests was 50 mL.min^{-1}. The heating ramp was set up at 20 °C.min^{-1} to ensure that the samples do not experience significant temperature or mass gradients, making the effect of mass and heat transfers negligible. After an isotherm of 120 min at 50 °C for thermal homogeneity, a heating rate of 20 °C.min^{-1} was applied from 50 to 800 °C. Each sample was tested twice to ensure repeatability of obtained results.

Difference weight loss curves were calculated (*Equation (1)*) in order to determine a potential increase or decrease in the thermal stability of the formulations, due to the incorporation of fillers in the system. These curves represent the difference between the experimental TG curve for the mixture ($w_{exp}(T)$) and the linear combination of TG curves ($w_{theo}(T)$) for the neat components (*Equation (2)*).

$$\Delta w(T) = w_{exp}(T) - w_{theo}(T) \quad (1)$$

$$w_{theo}(T) = 0.9 * w_{LF200} + 0.1 * w_{Fe_2O_3} \quad (2)$$

Where w_{LF200} and $w_{Fe_2O_3}$ are the experimental TG curves of the fluoropolymer resin and iron oxide respectively.

Table S3 Thermal stability characteristics of the formulations based on Lumiflon LF200 under N_2 and air with a heating rate of 20 °C.min^{-1}

		LF200	**LF200 + Fe_2O_3**
Under N2			
First step	**T_{onset} (°C)**	105	103
	T_{end} (°C)	287	235
	Resid. wt. (%) at T_{end}	95	94
Second step	**T_{onset} (°C)**	287	235
	T_{end} (°C)	800	800
	Resid. wt. (%) at T_{end}	16	28
Under Air			
First step	**T_{onset} (°C)**	115	109
	T_{end} (°C)	263	244
	Resid. wt. (%) at T_{end}	95	95
Second step	**T_{onset} (°C)**	263	244
	T_{end} (°C)	489	365
	Resid. wt. (%) at T_{end}	22	52
Thirdstep	**T_{onset} (°C)**	489	365
	T_{end} (°C)	636	559
	Resid. wt. (%) at T_{end}	0	9

To try to evidence the catalytic effect of iron oxide, thermogravimetric analyses (TGA) and difference weight loss calculations were performed on the dried fluoropolymer containing or not iron oxide. Only the fluoropolymer resin was considered, as it represents the upper layer of the coating containing the filler which is directly exposed to the flame (*Figure S4*).

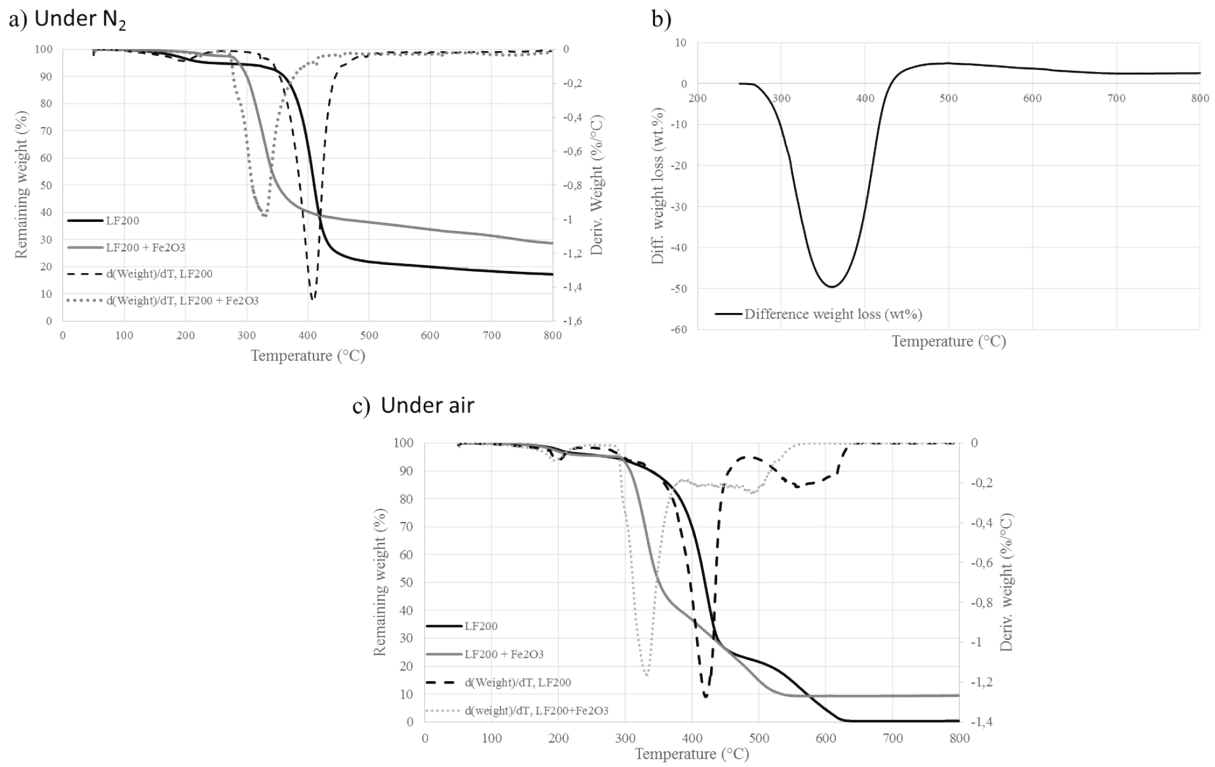

Figure S4. TG and DTG curves of Lumiflon LF200 and LF200 + Fe_2O_3 (a) under N2 and (c) under Air, and weight difference curves between experimental and calculated TG curves when Fe2O3 is added to the resin under N2 conditions (b)

Both systems degrade in two steps. But, in the presence of fillers, the second step starts at a lower temperature compared to the system without fillers (235°C vs 287°C). A higher amount of residue is also obtained in presence of Fe_2O_3: with an initial iron oxide loading of 10 wt. %, the residue left is 28%, compared to 16% without Fe_2O_3 (*Table S3*), higher to what was expected from the original inorganic addition. Under thermo-oxidative conditions, the amount of residue remaining at 800 °C is about 16 wt. % under nitrogen conditions, and 0 wt. % under air conditions (*Figure S4 c*). The fluoropolymer is therefore a charring material under pyrolytic conditions.

The difference weight loss curve allows highlighting the presence of specific interactions between polymer and additives depending on the temperature. It appears clearly that the addition of iron oxide induces an important thermal destabilization of the fluoropolymer resin between 270 and 420 °C (*Figure S4 b*). On the contrary, above 420°C, the experimental weight loss is slightly lower than expected: a stabilization step, ranging from 3 to 5 wt. % and related to the presence of iron oxide, is noticeable.

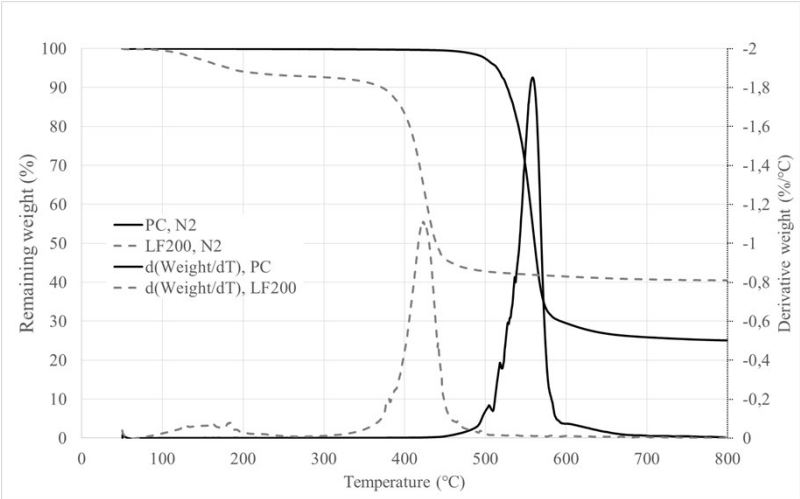

Figure S5. TG and DTG curves of PC and LF200 under N2 at 20°C/min

Table S4. Thermal stability characteristics of polycarbonate (PC) and Lumiflon LF200 under N_2 with a heating rate of 20 °C.min^{-1}

		PC	**LF200**
		Under N_2	
First step	**T_{onset} (°C)**	454	105
	T_{end} (°C)	800	287
	Resid. wt. (%) at T_{end}	25	95
Second step	**T_{onset} (°C)**	-	287
	T_{end} (°C)		800
	Resid. wt. (%) at T_{end}		16