Supplementary Information

Phosphorylated poly(vinyl alcohol) surface coatings as intumescent flame inhibitor for polymer matrix composites

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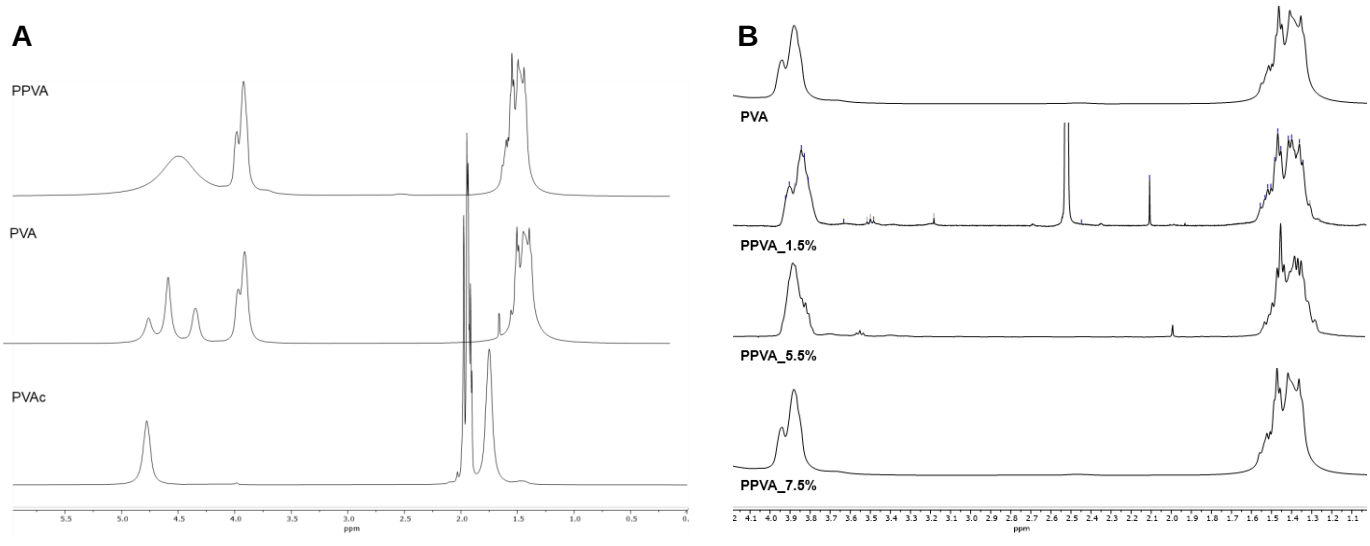

Figure S1: ^{1}H-NMR spectra of PVAc, PVA and PPVA_7.5% in d_6-DMSO (A); ^{1}H-NMR spectra of PVA and PPVA (1.5%, 5.5% and 7.5%) in d_6-DMSO (B)

The polymers obtained during the synthetic route were characterized by ^{1}H-NMR spectroscopy as reported in Figure S1. The NMR spectrum of poly(vinyl acetate) highlights the presence of the acetate group at 1.9 ppm and the signals related to the C-H and C-H_2 of the polymeric backbone at 1.7 ppm and 4.7 ppm, respectively. In the spectrum of the hydrolysed product (PVA), it's possible to observe the absence of acetate signals confirming the right functionalization of the polymer. Moreover, a shifting of the signals, derived from the chains protons, has been observed as well as an appearance of distribution at 4.7 ppm related to the alcoholic protons. The phosphorylated PVA spectrum (PPVA_1.5%, 5.5% and 7.5%), reported in Figure S1-B, did not allow to observing significant changes due to the absence of the characteristic signals derived from the new moieties presenting and the low functionalization degree.

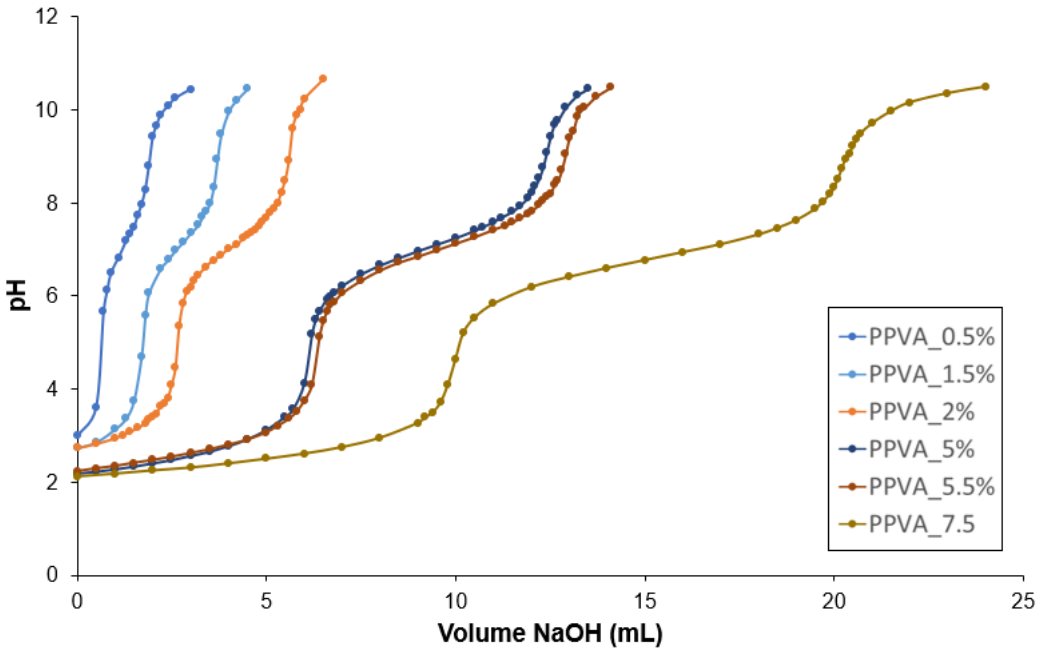

Figure S2: Titration curve related to PPVAs samples

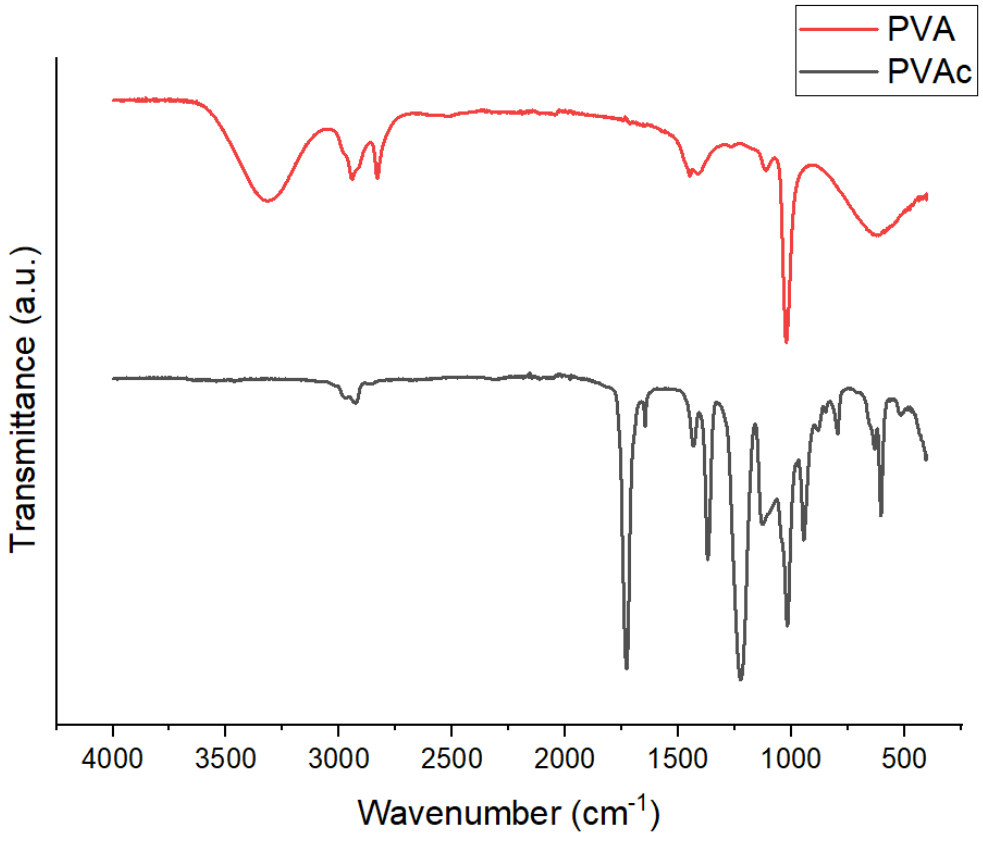

Figure S3: IR spectra of PVAc and PVA

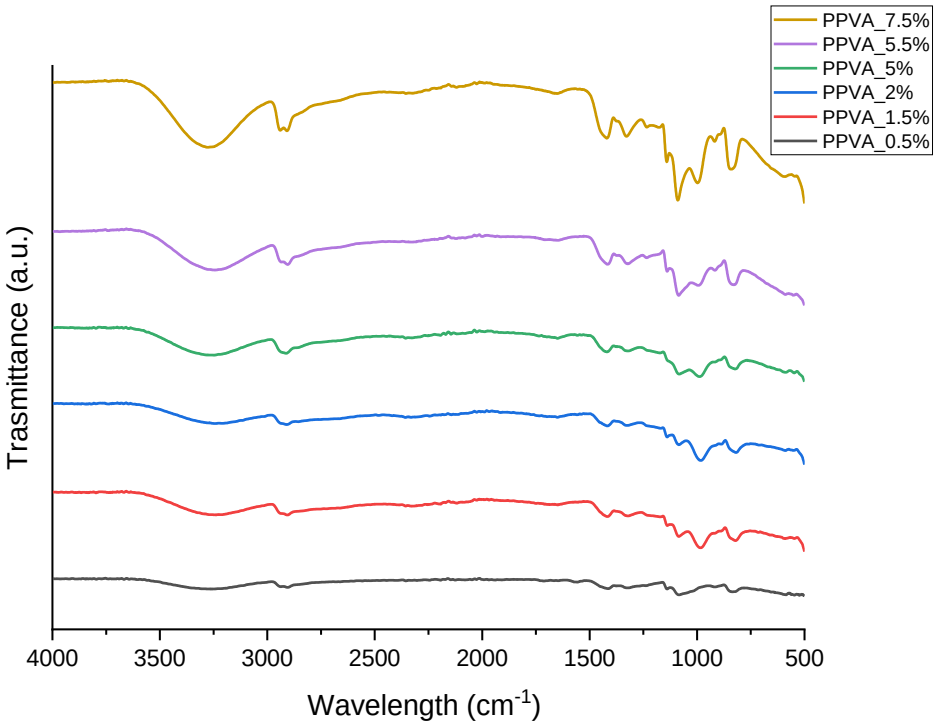

Figure S4: IR spectra of PPVA with different degree of phosphorylation (from 0.5% to 7.5% w/w)

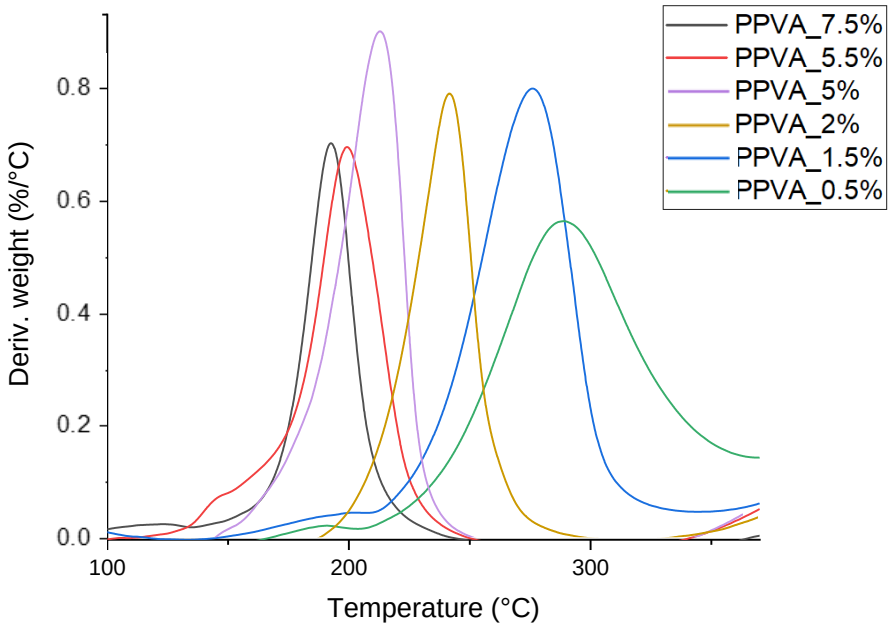

Figure S5: d-TGA thermograms of phosphorylated poly-vinyl-alcohol with different amount of phosphorus (0.5, 1.5, 2, 5, 5.5 and 7.5 %wt).

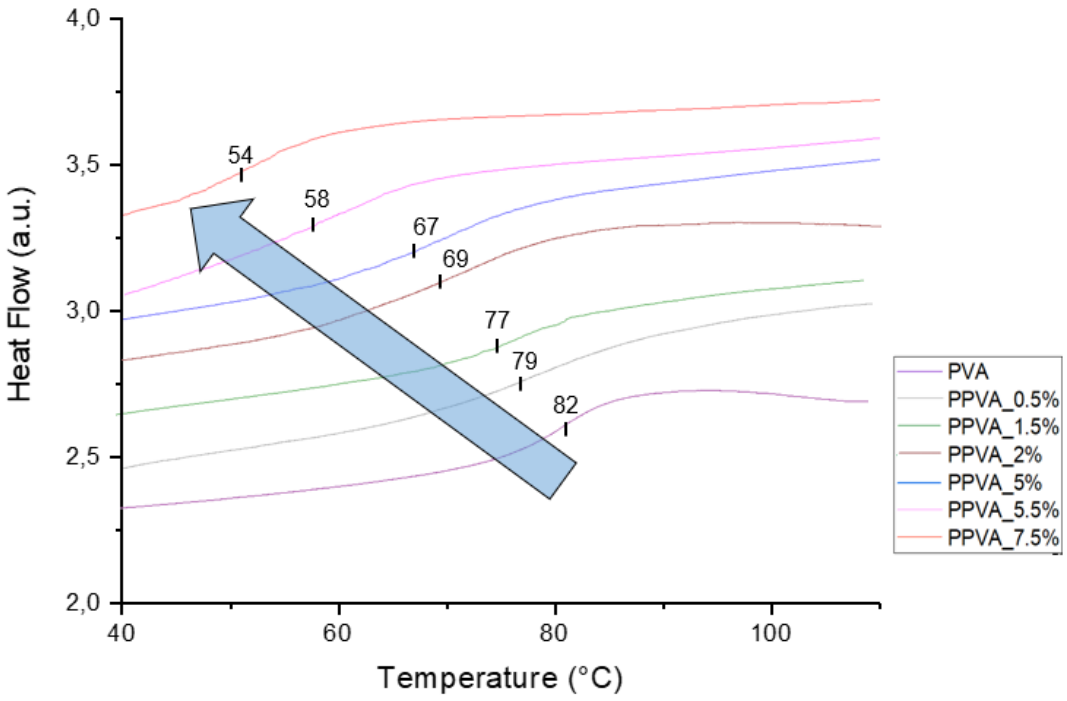

Figure S6: Differential Scanning Calorimetry thermograms related to phosphorylated poly(vinyl alcohol) with different amount of phosphorus (0.5, 1.5, 2, 5, 5.5 and 7.5 %wt).

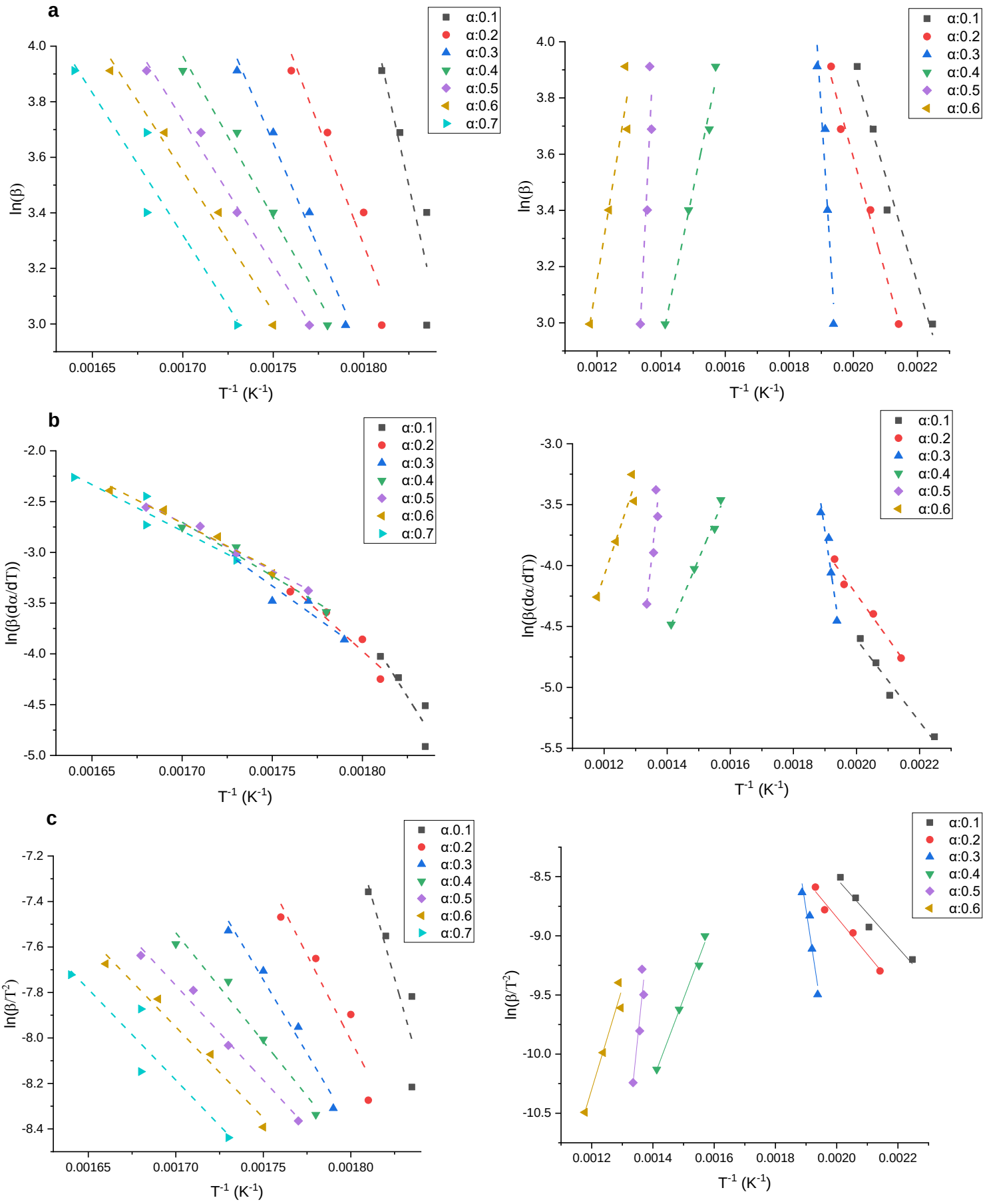

Figure S7: Kinetic curves related for the PVA and PPVA_7.5% samples applied FOW (a), Friedman (b) and KAS (c) methods

Fire testing of PVA-coated CFRPs

In order to verify that PVA does not affect flame retardancy or inhibition, cone calorimeter tests on the PVA-coated composite material (*CP-5_PVA*, *CP-10_PVA*, *CP-20_PVA* and *CP-40_PVA*) were also performed. The tests, made for the sake of comparison, were carried out with an incident heat flux of 35 kW/m^2, corresponding to a small-scale fire event.

The representative HRR curves and histogram results are shown in Figure S8 and listed in Table S1.

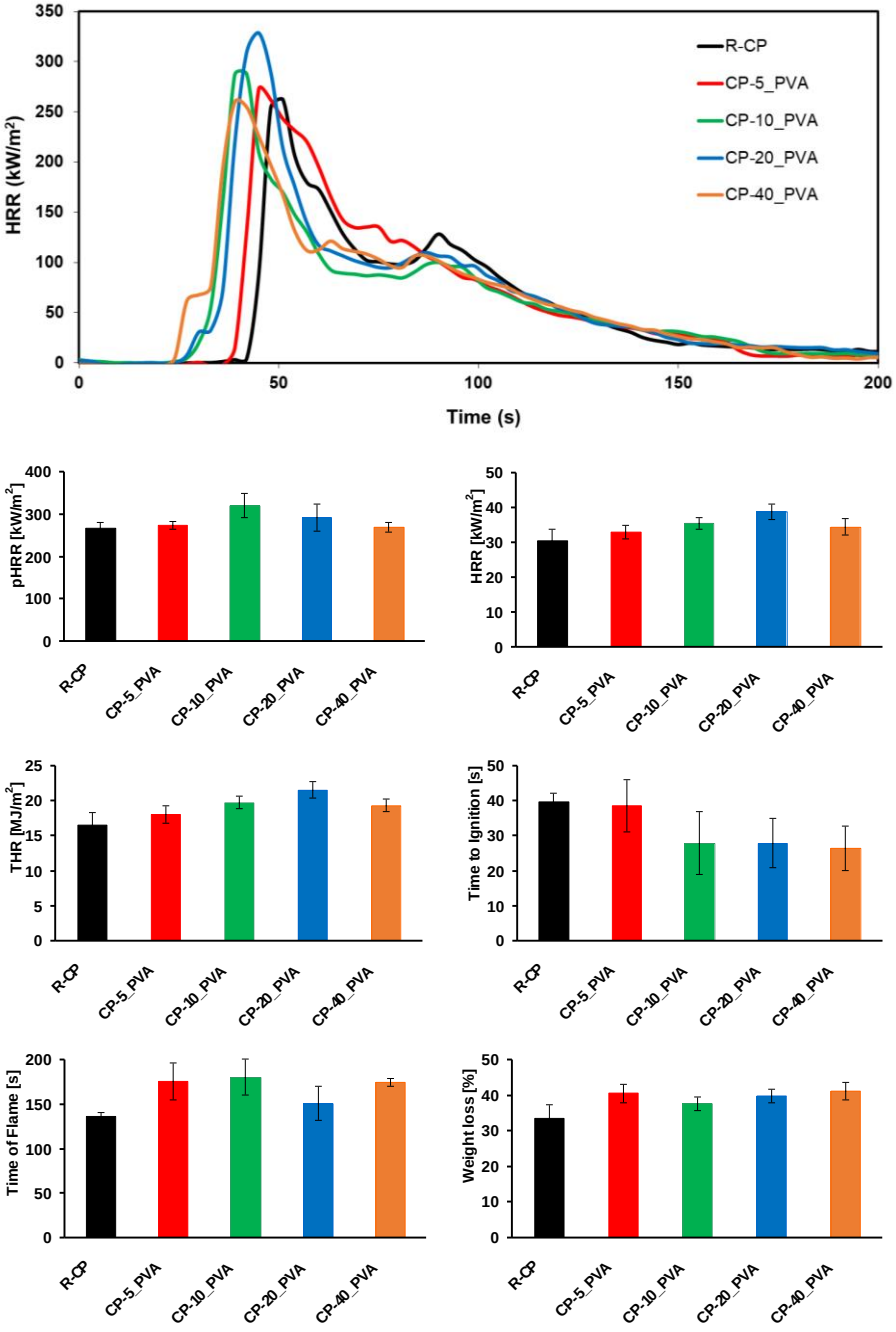

Figure S8: Representative HRR vs. time curves and cone-calorimeter histograms for samples tested at the cone-calorimeter: pHRR, mean HRR, THR, Time to Ignition, Time of Flame and Weight loss versus grammage. Colours: R-CP (uncoated CFRP, in black), CP-5_PVA (PVA 5 g/m^2, in red), CP-10_PVA (PVA 10 g/m^2, in green), CP-20_PVA (PVA 20 g/m^2, in blue), CP-40_PVA (PVA 40 g/m^2, in orange)

Table S1: Flame behaviour of composite panels uncoated and coated with PVA coating with different grammages, determined by cone-calorimeter measurements

Sample	***HRR*** [a] ***[kW/m²]***	***pHRR*** [b] ***[kW/m²]***	***TTP*** [c] ***[s]***	***THR*** [d] ***[MJ/m²]***	***TTI*** [e] ***[s]***	***TOF*** [f] ***[s]***	***W. L.*** [g] ***[%]***
R-CP	30.6 ± 3.3	268 ± 13	55 ± 10	16.6 ± 1.8	40 ± 3	137 ± 4	33.7 ± 3.8
CP-5_PVA	33.1 ± 1.9	274 ± 9	56 ± 12	18.1 ± 1.3	39 ± 7	176 ± 21	40.7 ± 2.6
CP-10_PVA	35.6 ± 1.7	320 ± 28	44 ± 6	19.8 ± 0.9	28 ± 9	181 ± 20	37.6 ± 1.9
CP-20_PVA	38.9 ± 2.1	293 ± 33	51 ± 8	21.6 ± 1.2	28 ± 7	151 ± 19	39.9 ± 1.9
CP-40_PVA	34.5 ± 2.4	270 ± 12	34 ± 11	19.4 ± 0.9	27 ± 6	175 ± 5	41.3 ± 2.5

[a] Average Heat Release Rate (HRR) is the irradiated thermic power released by the sample per square meter.
[b] Peak Heat Release Rate (pHRR) is the higher value of heat release.
[c] Time to Peak (TTP) is the time required to pHRR.
[d] Total Heat Release (THR) is the total heat released by the sample during the entire duration of the test.
[e] Time to Ignition (TTI) is the time needed for the first flame detection.
[f] Time of Flame (TOF) is the flame lifetime.
[g] Weight Loss (W. L.) is the amount of mass loss during the test.

Concerning the PPVA-coated panels, completely different considerations can be made about the pure PVA-coated composite material (Figure S8 and Table S1).

Results obtained showed that the presence of the pure PVA significantly worsen the flame properties of the composite material: increases in the HRR mean, THR and, in particular, in the Time Of Flame (TOF) value, were indeed observed.

As anticipated before and as clear from the histograms in Figure S8, increasing the grammage from 5 g/m^2 to 40 g/m^2 did not modify the results and did not modify the flame behaviour of the coated composite materials.