

Layer-by-layer-assembled chitosan/phosphorylated cellulose nanofibrils as a bio-based and flame protecting nano-exoskeleton on PU foams

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1 Layer by Layer-Assembled Chitosan/Phosphorylated
2 Cellulose Nanofibrils as a Bio-based and Flame
3 Protecting Nano-exoskeleton on PU foams

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20 Abstract

21 The layer-by-layer (LbL) assembly of chitosan (CH) and phosphorylated cellulose nanofibrils (P-
22 CNF) is presented as a novel, sustainable and efficient fire protection system for polyurethane
23 foams. The assembly yields a linearly growing coating where P-CNF is the main component and is
24 embedded in a continuous CH matrix. This CH/P-CNF system homogenously coats the complex 3D
25 structure of the foam producing a nano-exoskeleton that displays excellent mechanical properties
26 increasing the modulus of the foam while maintaining its ability of being cyclically deformed.
27 During combustion the CH/P-CNF exoskeleton efficiently prevents foam collapse and suppresses
28 melt dripping while reducing the heat release rate peak by 31% with only 8% of added weight. The
29 coating behavior during combustion is investigated and correlated to the observed performances.
30 Physical and chemical mechanisms are identified and related to the unique composition and
31 structure of the coating imparted by the LbL assembly.

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34 **KEYWORDS:** layer by layer; chitosan; phosphorylated cellulose nanofibril; polyurethane foams;
35 thermal stability; flame retardancy

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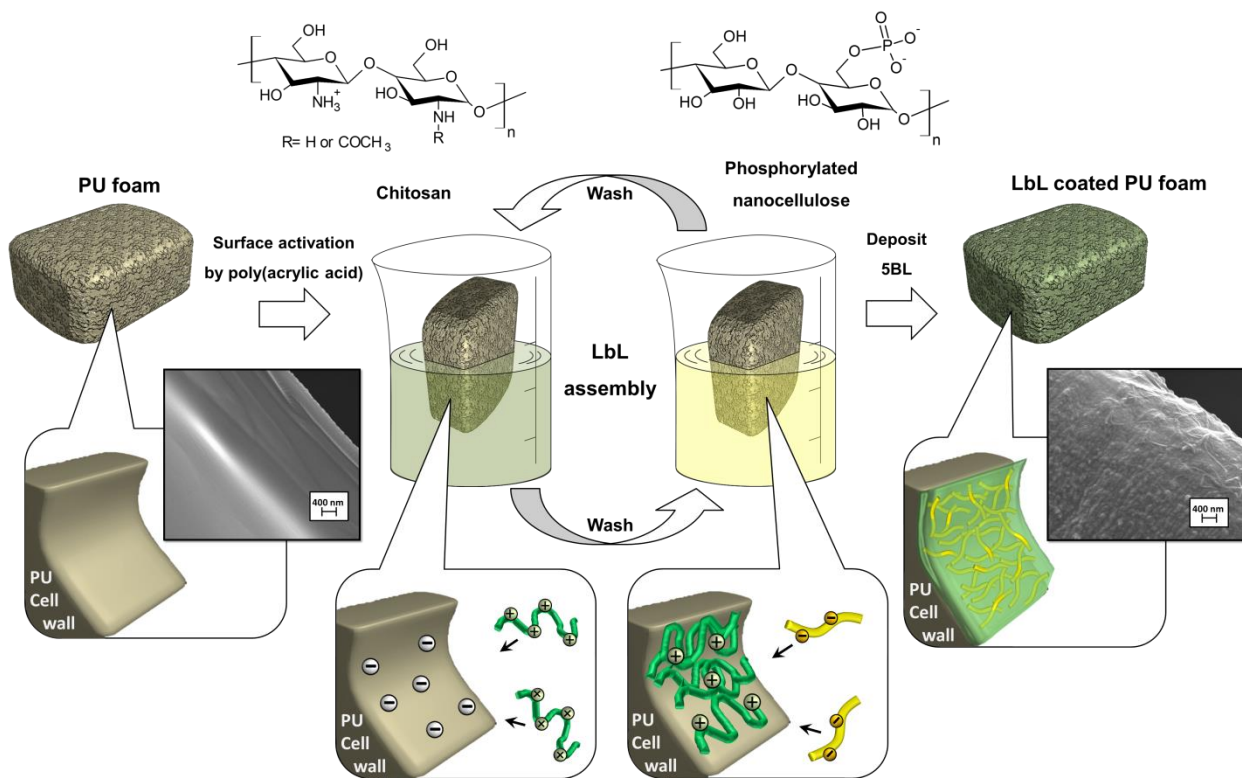
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45 INTRODUCTION

46 In recent years, the scientific community has focused significant efforts on the use of bio-based
47 resources for the production of functional materials capable of meeting current societal demands for
48 green and sustainable alternatives. The fire protection of materials represents an area of great
49 concern. Indeed, due to recently perceived environmental problems, some of the currently adopted
50 chemicals and treatments (defined flame retardants) have been under regulatory scrutiny and
51 subsequently either banned or strongly limited in their applications. (Stieger, Scheringer, Ng, &
52 Hungerbuhler, 2014) This situation creates a strong demand for new, high performing and
53 environmentally friendly fire protection solutions. Recently, it has been demonstrated that
54 deoxyribonucleic acid (DNA) extracted as by-product from fish production can be employed to
55 deliver efficient flame retardant solutions. (J. Alongi, Carletto, et al., 2013) (J. Alongi, Di Blasio,
56 Cuttica, Carosio, & Malucelli, 2014) (Carosio, Cuttica, Di Blasio, Alongi, & Malucelli, 2015)
57 (Jenny Alongi, Cuttica, & Carosio, 2016). Beside DNA, nature can offer other bio-based building
58 blocks such as chitosan and nanofibrillated cellulose (CNF) that are characterized by a much larger
59 availability and sustainability. Indeed, chitosan can be produced by deacetylation of chitin extracted
60 from crab shells while CNF can be conveniently extracted from wood fibers, or other cellulose
61 containing materials, yielding fibrils with typical dimensions of 3-15 nm in diameter and 0.7-3
62 micrometers in length. (Dash, Chiellini, Ottenbrite, & Chiellini, 2011) (Klemm et al., 2011) CNF
63 represents one of the newest and most interesting bio-based building blocks for material preparation
64 and it is currently studied in a wide variety of application fields.(Lavoine, Desloges, Dufresne, &
65 Bras, 2012) (Jorfi & Foster, 2015) (Du, Zhang, Liu, & Deng, 2017) Both chitosan and CNF possess
66 interesting key features that make them appealing for the construction of functional flame resistant
67 materials. For instance, chitosan has been employed as cationic polyelectrolyte for the layer-by-
68 layer (LbL) assembly of highly flame retardant and nanostructured thin films. (Leistner, Abu-Odeh,
69 Rohmer, & Grunlan, 2015) (Cain et al., 2014) (Carosio & Alongi, 2016b) (Koklukaya, Carosio, &
70 Wägberg, 2017) This technique simply consists in the alternate adsorption of chemical species on a

71 substrate on the basis of both specific and nonspecific interaction (e.g. electrostatic attraction
72 between polyions and/or nanoparticles) yielding stratified or highly interpenetrated nanostructured
73 coatings. (Decher, 1997) On the other hand, water-based CNF colloids have been processed using
74 simple paper-making approaches to produce nanostructured films with peculiar mechanical and
75 physical properties including optical transparency, gas barrier properties and flame retardancy
76 characteristics. (Henriksson, Berglund, Isaksson, Lindstrom, & Nishino, 2008) (Liu & Berglund,
77 2012) (Carosio, Kochumalayil, Cuttica, Camino, & Berglund, 2015) Recently, we have reported the
78 preparation of phosphorylated cellulose nanofibrils (P-CNF): an inherently flame retardant version
79 of CNF that can be used in water-based processes to prepare strong nanosheets with self-
80 extinguishing and non-ignitability properties. (Ghanadpour, Carosio, Larsson, & Wagberg, 2015)
81 In this paper we are applying the LbL assembly of chitosan and P-CNF for the production of
82 nanostructured fire shielding thin films capable of protecting dense (100 g/dm^3) open cell
83 polyurethane foams (PU). PU foams are often referred to as the principal cause for fire initiation
84 and spreading to other materials due to melt dripping and hence represent a substrate in strong need
85 for novel and efficient fire protection solutions. (Hirschler, 2008) (Hammel et al., 2017) (Cho et al.,
86 2015) (Xu, Yu, & Qian, 2017) The study of this CH/P-CNF assembly as well as its application to
87 PU foams has never been reported before and represents a novel example of a fully renewable and
88 nature-based FR solution. The LbL assembly poses further advantages with respect to conventional
89 approaches allowing for the use of a green and sustainable technique that operates with diluted
90 water-based suspension/solution at room conditions under pHs between 4 and 9. Figure 1 shows a
91 schematic representation of the approach proposed in this paper.



92

93 **Figure 1.** Schematic representation of the LbL process exploited in this manuscript. PU foams are
 94 pre-activated by poly(acrylic acid) and then alternatively dipped in the chitosan (positive) and
 95 phosphorylated cellulose nanofibrils (negative) baths. The process is repeated 5 times in order to
 96 deposit 5 Bi-Layers (BL). (Note that the components in the images are not drawn to scale).

97 The LbL assembly of CH and P-CNF has been evaluated by investigating the coating composition
 98 and morphology. The hypothesis is that the LbL allows for unique compositional and structural
 99 features that subsequently result in synergistic rather than additive interactions between the chitosan
 100 and P-CNF. CH can act as the continuous matrix embedding the anionic P-CNF which can enhance
 101 the coating char formation, during combustion, allowing for the production of protective thermally
 102 stable carbonaceous structures. (Carosio, Alongi, & Malucelli, 2012) To verify this, the LbL
 103 assembled CH/P-CNF coating has been studied as a standalone material evaluating its thermal and
 104 thermo-oxidative stability as well as the structural and chemical changes resulting from the
 105 exposure to a heat source. The achieved results have then been related to the coating performances
 106 on foams. The approach developed in this paper allows for a better understanding of the

107 structure/property relationship in FR-LbL assemblies and poses the base for the design of more
108 efficient FR solutions consisting of sustainable resources

109 **2. Experimental Details**

110 *2.1 Materials:* open cell polyurethane foams (PU) (100 g/dm^3 , thickness of 15 mm) have been
111 supplied by Compart (France). Poly(acrylic acid) (average $M_w \sim 100000$, 35 wt. % in H_2O),
112 branched poly(ethylene imine) (BPEI, $M_w \sim 25,000$ by Laser Scattering, $M_n \sim 10,000$ by Gel
113 Permeation Chromatography, as reported in the material datasheet), were purchased from Sigma
114 Aldrich (Milwaukee, WI). Chitosan (CH, $M_w \sim 60,000$, 95% deacetylation) was purchased from
115 GTC Union Corp., Qingdao, China. Poly(diallyldimethylammonium chloride) (PDADMAC,
116 solution, $M_w 400,000 - 500,000$, 50 wt.% in H_2O) was purchased from Sigma Aldrich. The
117 polymer was purified by dialysis followed by freeze-drying prior to use. Poly(vinylsulfate
118 potassium) (KPVS colloidal titration grade, solution, M_w of the repeating unit 162.21, N/400 in
119 H_2O) was purchased from Wako Pure Chemical Industries, Ltd. and diluted with Milli-Q water
120 prior to use The P-CNF gel used in this work was obtained from the phosphoryl functionalized
121 fibers based on a previously described procedure. (Ghanadpour et al., 2015) The P-CNF dispersion
122 to be used in LbL assembly was prepared by diluting a 2 wt.% gel in Milli-Q water followed by
123 ultra-sonication for 10 min at 40% amplitude using a Sonics & Materials, Inc. Vibra-cell equipped
124 with a titanium probe. The aggregated and non-fibrillated fiber fragments were then removed by
125 centrifugation at 4,500 rpm for 1 h and the supernatant was collected as the stable P-CNF
126 dispersion. PAA was employed as 1 wt.-% water solution, while BPEI, CH, P-CNF were used at
127 0.1 wt.-%. The water employed was a $18.2 \text{ M}\Omega$ deionized water supplied by a Q20 Millipore
128 system (Milano, Italy). The pH of PAA and BPEI were used at their unmodified pH of 3 and 10,
129 respectively. CH was firstly dissolved at pH 2 and then pH was adjusted to 5. The ionic strength of
130 the solution was changed by adding 10 mM NaCl. The pH of the P-CNF suspension was adjusted
131 to 6. Solutions of 2M HCl and 1M NaOH were employed to adjust the pH.

132 *2.2 Layer by Layer deposition on Si Wafers:* before LbL deposition, the surface of Si wafers was
133 activated by 5 min dipping in a 0.1 wt.-% BPEI solution, washed with deionized water and dried
134 with compressed air. Then, the Si wafer was alternately dipped into the P-CNF and CH solutions in
135 order to deposit one bi-layer repetitive unit. The deposition time was set to 15 min for P-CNF and
136 10 min for CH. After each adsorption step the silicon wafer was washed with deionized water. An
137 automatic dipping robot (StratoSequence VI, nanoStrata Inc., Tallahassee, FL, USA) was used to
138 fabricate a 150BL film for structural and post combustion analyses.

139 *2.3 Layer by layer deposition on PU foams:* before the deposition, the foams were dipped and
140 squeezed in deionized water in order to remove dust and residual cell walls and then dried in an
141 oven (80°C). Then, the foams were firstly dipped in 1 wt.-% PAA solution with pH 3 for 10 min.
142 Following this activation step, the foams were alternately dipped in the CH and P-CNF solution
143 until 5 BL were formed. The dipping time for CH was set to 10 min whereas it was increased to 15
144 min for P-CNF. After each deposition step, the foams were carefully squeezed and washed by
145 dipping in deionized water for 5 min. At the end of the process, the treated foams were dried in an
146 oven at 80°C.

147 *2.4 Characterization*

148 *Fourier transformed-infrared spectroscopy (FT-IR):* the growth of the LbL assembly was
149 monitored using a Frontier FT-IR/FIR spectrophotometer (16 scans and 4 cm⁻¹ resolution, Perkin
150 Elmer, Milano, Italy). IR spectra were acquired, at room temperature, after each deposition step.

151 *Fourier transformed-infrared spectroscopy in attenuated total reflectance (FT-IR ATR):* spectra in
152 the range 4000-700cm⁻¹ (16 scans and 4cm⁻¹ resolution) were collected at room temperature using a
153 FT-IR/FIR spectrophotometer (Perkin Elmer mod. Frontier, Waltham, MA, USA) equipped with a
154 diamond crystal.

155 *Raman spectroscopy:* raman spectra were performed on a InVia Raman Microscope (Renishaw,
156 argon laser source 514 nm/50mW, 10 scans) coupled with a Leica DM 2500 optical microscope.

157 *Quartz crystal microbalance with dissipation (QCM-D)*: the LbL build-up of the CH/P-CNF
158 assembly was also monitored by QCM-D (E4, Q-Sense AB, Västra Frölunda, Sweden) using a
159 method described in detail elsewhere. (Rodahl, Höök, Krozer, Brzezinski, & Kasemo, 1995) The
160 AT-cut quartz crystal sensors with silicon oxide coating were also purchased from Q-Sense AB and
161 were plasma cleaned for 2 min at 30 W, immediately before use. This QCM-D technique allows for
162 simultaneous measurement of the change in resonance frequency (Δf) and energy dissipation (D) of
163 the QCM crystal upon adsorption to the crystal surface. The normalized frequency change is
164 directly proportional to the sensed mass, which corresponds to both the adsorbed species and the
165 associated water, according to the Sauerbey relation:

$$166 \quad \Delta m = C\Delta f/n \quad \text{Eq. 1}$$

167 where Δm is the change in the adsorbed mass per area, C is the mass sensitivity constant (-0.177
168 mg/m²Hz), Δf is the change in frequency and n is the number of the overtone. The energy
169 dissipation can be related to the viscoelastic properties of the adsorbed layer. (Aulin, Varga,
170 Claesson, Wågberg, & Lindström, 2008)

171 *Polyelectrolyte titration*: the amount of CH and P-CNF adsorbed onto the PU foam in each layer
172 deposition was determined by polyelectrolyte titration of the residual CH or P-CNF in the solution
173 after the adsorption. A combination of a Metrohm 716 DMS Titrino titrator and a Particle Metrix
174 Stabino stability analysis system was used, where CH was titrated by negatively charged
175 polyvinylsulfate potassium (KPVS) and P-CNF was titrated by positively charged
176 polydiallyldimethylammonium chloride (PDADMAC).

177 *Field Emission-Scanning Electron Microscopy (FE-SEM)*: surface morphology of untreated and
178 LbL treated foams was investigated using a Field Emission-Scanning Electron Microscopy ZEISS,
179 FEG model MERLIN (beam voltage: . The cross section of Si wafers was obtained by fragile
180 fracture of the substrates, while untreated and LbL treated foams were cut in small pieces (10 x 10 x
181 5 mm³). The resulting samples were placed on conductive adhesive tapes and chromium-metallized.

182 *Thermogravimetric analysis (TGA):* thermogravimetric analysis under nitrogen atmosphere (gas
183 fluxes of 60 and 40 ml/min for sample gas and balance protection gas, respectively) was performed
184 by a TAQ500 of Waters-TA Instruments (Milano, Italy). The sample (approx. 10 ± 0.5 mg) was
185 placed in open alumina pans and heated from 50 to 800°C using a heating rate of 10°C/min.
186 $T_{\text{onset}10\%}$ (temperature at 10% of weight loss), T_{max} (temperature at maximum rate of weight loss),
187 and residue at 800°C were obtained by these measurements.

188 *Mechanical properties:* compression stress/strain measurements were performed with
189 approximately 1 cm³ untreated and LbL-coated PU foams, using the Instron 5944 (Instron
190 Corporation, High Wycombe, UK) instrument equipped with a 500 N load cell. The foam samples
191 were cyclically compressed between two metallic plates up to 90% strain, using a strain rate of 10
192 %/min during the three applied cycles. The samples were conditioned prior to the test at 23 °C and
193 50% R.H. and the test was repeated at least 5 times for each formulation in order to ensure
194 reproducibility.

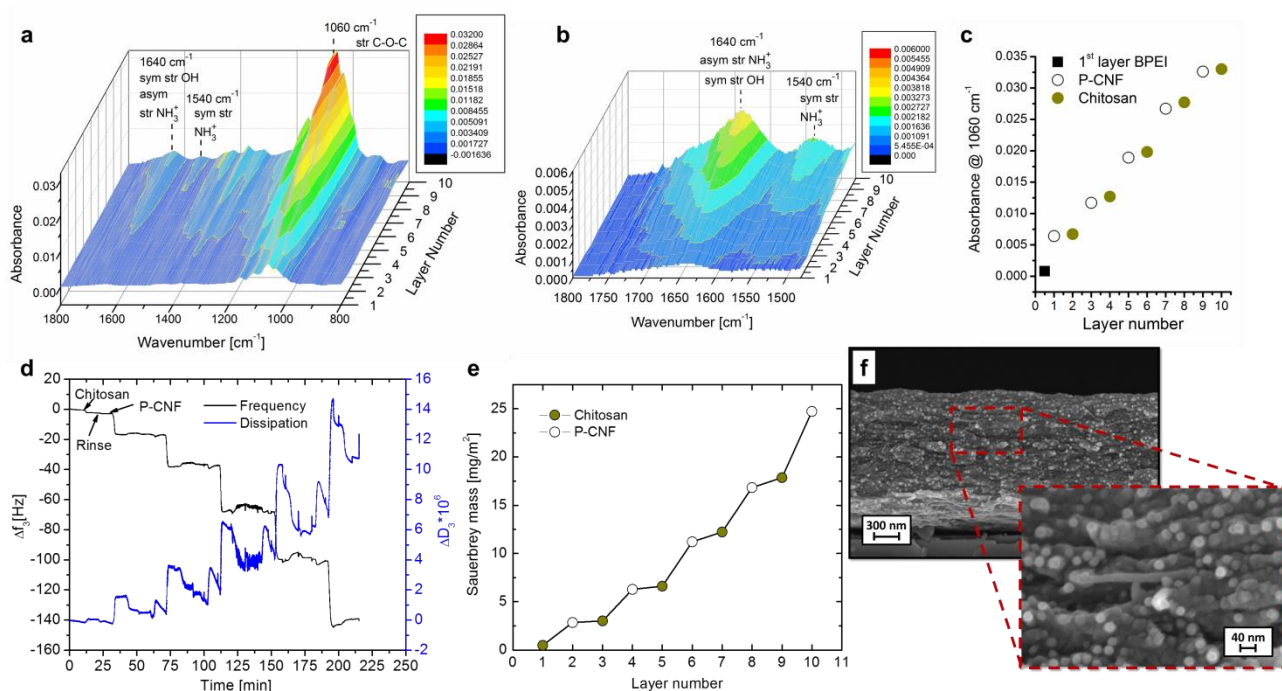
195 *Flammability:* the flammability of prepared samples has been tested in horizontal configuration
196 following the ASTM D 4986 standard. The sample (30 x 100 x 15 mm³) was positioned on a
197 metallic grid and ignited from its short side by a 20 mm blue methane flame (flame application
198 time: 6 s). Dry cotton wad was placed 30 cm underneath the metallic grid in order to evaluate the
199 occurrence of the melt dripping phenomenon. Each test was repeated 3 times for each formulation
200 in order to ensure reproducibility; during the test, parameters such as burning rate, final residue and
201 formation of incandescent droplets of molten polymer were registered.

202 *Cone calorimetry:* cone calorimetry (Fire Testing Technology, FTT, UK) was employed to
203 investigate the combustion behavior of untreated and LbL-treated foams (50 x 50 x 15 mm³) under
204 35kW/m² in horizontal configuration, following the ISO 5660 standard. The following parameters
205 were registered: Time To Ignition (TTI, [s]), peak of Heat Release Rate (pkHRR, [kW/m²]), Total
206 Heat Release (THR, [MJ/m²]), and final residue (%). Before flammability and cone calorimetry
207 tests, samples were conditioned for at least 24 hours in a climatic chamber (23°C, 50% R.H.)

208 **3. Results and discussion**

209 *3.1 Coating growth by FT-IR spectroscopy and QCM-D using SiO₂ surfaces*

210 Each layer constituent has been firstly evaluated by FT-IR spectroscopy (*see* Figure S1 in
 211 Supporting Information). Neat chitosan shows characteristic signals related to NH₃⁺ asymmetric
 212 (1624 cm⁻¹) and symmetric (1522 cm⁻¹) stretching, C-O-C stretching of the glycosidic linkage at
 213 1090 cm⁻¹ and CH₂ groups (1450-1300 cm⁻¹). (Socrates, 2006) Similar to CH, the most intense peak
 214 of pure P-CNF is ascribed to C-O-C groups from glycosidic units or from β-(1→4)-glycosidic
 215 bonds (1060 cm⁻¹); the presence of the phosphate functionalization is highlighted by minor
 216 peaks/shoulders associated to P-O (966 and 928 cm⁻¹) and P=O (1234 cm⁻¹) groups.(Ghanadpour et
 217 al., 2015) (Socrates, 2006) The layer by layer growth of CH and P-CNF can be easily followed by
 218 IR spectroscopy, as reported in Figures 2 a, 2 b and 2 c displaying the 3D projection of the
 219 restricted IR regions and the intensity of the peak at 1060 cm⁻¹ plotted as a function of BL number.



220

221 **Figure 2.** Characterization of the build-up of CH/P-CNF assembled on SiO₂ surfaces by using IR

222 and QCM: (a) and (b) 3D projection of restricted IR region, (c) intensity of the IR signal at 1060

223 cm^{-1} as function of deposited BL number, (d) change in normalized frequency and energy
224 dissipation through the multilayer build-up, (e) total adsorbed mass of multilayer film calculated
225 using the Sauerbrey model and (f) FE-SEM micrographs of Si wafer cross section of the coating at
226 150 BLs.

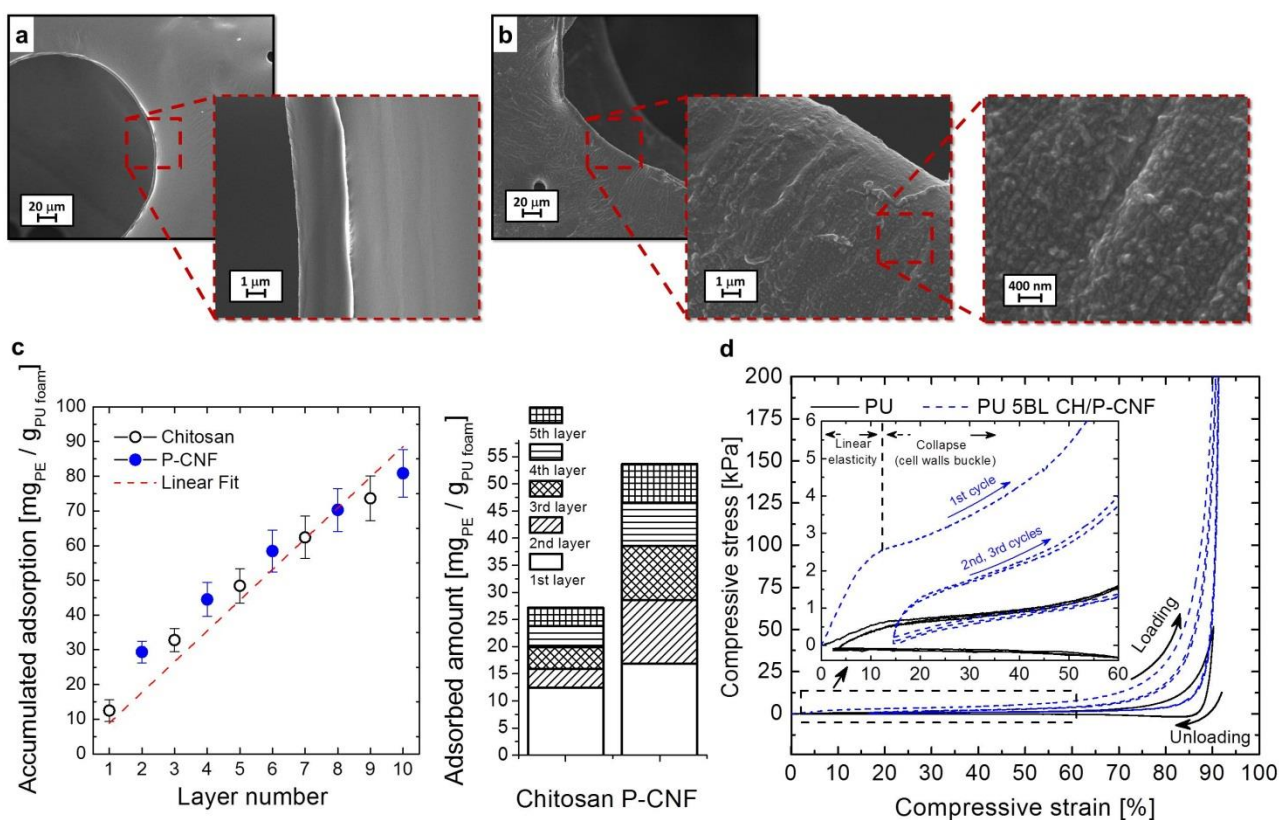
227 The characteristic peaks of CH and P-CNF grow proportionally with the number of deposited BL,
228 as observed for neat components the most intense peak is found in the 1100-1000 cm^{-1} region and is
229 ascribed to C-O-C stretching vibration of the glycosidic linkage. This latter peak is centered at 1060
230 cm^{-1} indicating a major contribution from P-CNF. The presence of CH is evidenced by NH_3^+ signals
231 at 1640 and 1540 cm^{-1} (Figure 2 b); it is worth mentioning that such signals are shifted to higher
232 wavenumbers with respect to pure CH (*compare* Figure S1) as a consequence of the ionic
233 interactions established with the negatively charged phosphate groups. The intensity of the peak at
234 1060 cm^{-1} reveals a linear growth for this CH/P-CNF assembly. This signal increases more steeply
235 after the deposition of P-CNF thus indicating this latter as being the main component of the coating.

236 The LbL build-up has also been studied in situ by QCM-D measurements and Figure 2 d reports the
237 shift in normalized resonance frequency (3rd overtone) and energy dissipation as a function of time
238 for the sequential adsorption of CH and P-CNF onto the silicon oxide substrate up to 5 BL. A
239 decrease in resonance frequency indicates adsorption while an increase may refer to desorption of
240 solid material or a change in the solvent content of the adsorbed layer. (Aulin et al., 2008) A steady
241 multilayer film build-up is illustrated by the step-wise decrease in frequency values with P-CNF
242 adsorption being significantly higher than CH, in agreement with IR results. This may be explained
243 by the lower charge density of P-CNF compared to CH (545 vs. 6740 $\mu\text{eq/g}$ respectively) where less
244 amount of chitosan is required to neutralize the negatively charged phosphorylated
245 fibrils.(Schlenoff, Ly, & Li, 1998) The LbL assembly is associated with a rather low energy
246 dissipation implying the formation of rather thin and rigid layers. (Ghanadpour, Carosio, &
247 Wågberg, 2017) The amount of adsorbed mass on the QCM crystal upon each layer deposition

248 calculated using Eq. 1 is reported in Figure 2 e. As expected, the increase in mass is higher due to
 249 P-CNF adsorption, which again is in agreement with IR results and indeed reveals the dominance of
 250 the phosphorylated fibrils within the formed multilayer film. FE-SEM observations performed for
 251 the cross sections of a 150 BL coating deposited on Si wafer highlight the dense and compact nature
 252 of this assembly (Figure 2 f). CH acts as continuous matrix embedding P-CNF nanofibrils that are
 253 clearly visible at high magnifications.

254 3.2 Coating assembly on PU foams, morphology, mechanical and flame retardant properties

255 Following the results described in the previous section, 5BLs of CH/P-CNF assembly have been
 256 deposited on PU foams. Low and high magnification FE-SEM observation of neat and LbL-coated
 257 foams are reported in Figures S2 and 3, respectively.



258

259 **Figure 3.** Summary of the LbL treatments of PU foams shown as FE-SEM micrographs of

260 uncoated (a) and LbL-coated (b) PU foams, (c) amount adsorbed on PU foam at each deposition

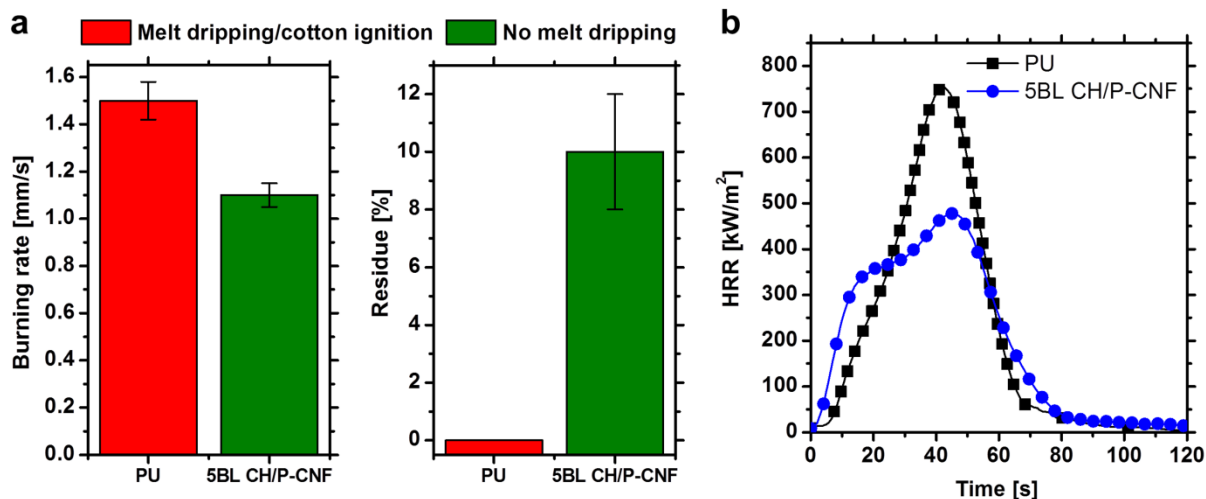
261 step evaluated by polyelectrolyte titration and (d) compression tests on uncoated and LbL-coated
262 foams.

263 The neat PU foam shows a characteristic open cell structure with walls characterized by a smooth
264 and even morphology (Figures S2 a and 3 a). Such morphology is clearly changed by the LbL
265 deposition. Indeed, coated PU clearly shows the formation of a thin and homogeneous coating that
266 extends through the complex 3D structure of the foam. High magnification micrographs clearly
267 demonstrates the nanotexture of the assembly that, similarly to what observed on model Si wafer
268 (Figure 2 f), consist of P-CNF embedded within a CH matrix. From morphological observation it is
269 apparent that the deposited LbL coating results in a continuous and thin exoskeleton that follows the
270 PU structure, easily conforming at the edges of the cell walls without altering its open cell nature
271 (Figure S2). Polyelectrolyte titration was employed in order to evaluate the adsorbed amount of the
272 coating constituents on PU foam after each deposition step; the plot reported in Figure 3 c clearly
273 points out a linear growth where the adsorption of P-CNF results in a more steep increase in mass
274 with respect to CH, especially for the initial layers of the coating. The evaluation of the total
275 adsorbed mass on PU foam (Figure 3 c) indicates an average add-on of 8 wt.-% after 5 BLs with P-
276 CNF as the main component of the coating (66 wt.-%). These results corroborate what observed on
277 model Si and quartz surface by IR spectroscopy and QCM-D measurements, respectively (Figures 2
278 c and 2 e). The effect of the coating on the foam mechanical properties has been evaluated by
279 compression testing. Figure 3 d shows the stress-strain curve for three subsequent compression
280 cycles performed with the unmodified and the LbL-coated foams. When the foam is compressed,
281 the resulting stress-strain curve normally shows three regions. At low strains, the foam deforms in a
282 linear-elastic way; then, there is a plateau of deformation at almost constant stress, followed by a
283 region of densification where the stress quickly increases as the cell walls crush together. Upon
284 unloading the foam recovers the shape by returning to the original dimensions and shape. The
285 unmodified PU follows this trend during three loading/unloading cycles. A similar behavior can be
286 observed for the LbL-treated foams; however, as reported in Figure 3 d and its inset, the loading

287 stress values are higher than for the unmodified foam and, after the first compression, the foam is
288 capable of recovering only a fraction of deformation. A similar behavior has been already observed
289 for LbL-treated foams and is ascribed to the effect of the first cycle that by exerting a compression
290 stress on the freshly deposited coating forces its compliance with the PU deformation. (Li, Kim,
291 Shields, & Davis, 2013) This induces the formation of small cracks in the LbL coating and reduces
292 its stiffness thus allowing, during subsequent cycles, for a typical hysteresis curve with a complete
293 recovery of the deformation. Further cycles do not alter the mechanical properties of the coated
294 foams as demonstrated by the second and the third cycles that lay overlapped. This can be also
295 appreciated by observing the data showing the compressive stress as a function of time (Figure S3).
296 The higher stress values required to deform the foam indicate that the first cycle only partially
297 reduces the stiffness of the LbL coating that maintains a good adhesion to the foam and results in a
298 firmer foam. These results further indicate the homogeneity of the coating that, being deposited on
299 each available surface, is capable of modifying the mechanical properties of the foam while
300 maintaining its flexibility. Thanks to the ionic interactions occurring at molecular scale within the
301 LbL assembly and the high strength of the fibrils this CH/P-CNF coating is capable of modifying
302 the PU mechanical properties with only 8 wt.-% of mass added. (Ghanadpour et al., 2017)

303 *3.3 Evaluation of the effect of the LbL coating on flame retardant properties of the PU foams*

304 Treated and untreated PU foams have been subjected to flammability (reaction to a direct flame
305 application) and cone calorimetry (exposure to a heat flux) tests. Both tests represent
306 complementary approaches capable of evaluating the efficiency of the coating in reducing the well-
307 known fire threat of PU foams. Figure 4 summarizes data from flammability and cone calorimetry
308 tests; for the latter, HRR plots as a function of time for untreated and LbL-treated PU is reported.
309 Table 1 collects the complete sets of cone calorimetry data.



310

311

Figure 4. Burning rates and final residues evaluated by flammability tests in horizontal configuration (a) and heat release rate (HRR) plots as function of time measured by cone calorimetry tests (b).

312

313

Table 1. Cone calorimetry data of untreated and LbL-treated PU foams.

Sample	TTI $\pm \sigma$ [s]	Av. HRR $\pm \sigma$ [kW/m ²]	pkHRR $\pm \sigma$ [kW/m ²]	THR $\pm \sigma$ [MJ/m ²]	TSR $\pm \sigma$ [m ² /m ²]	Residue $\pm \sigma$ [%]
PU	11 \pm 7	154 \pm 21	718 \pm 70	24.3 \pm 0.6	430 \pm 13	6 \pm 1
5 BL CH/P-CNF	9 \pm 1	136 \pm 11	494 \pm 20	23.6 \pm 0.5	470 \pm 30	7 \pm 1

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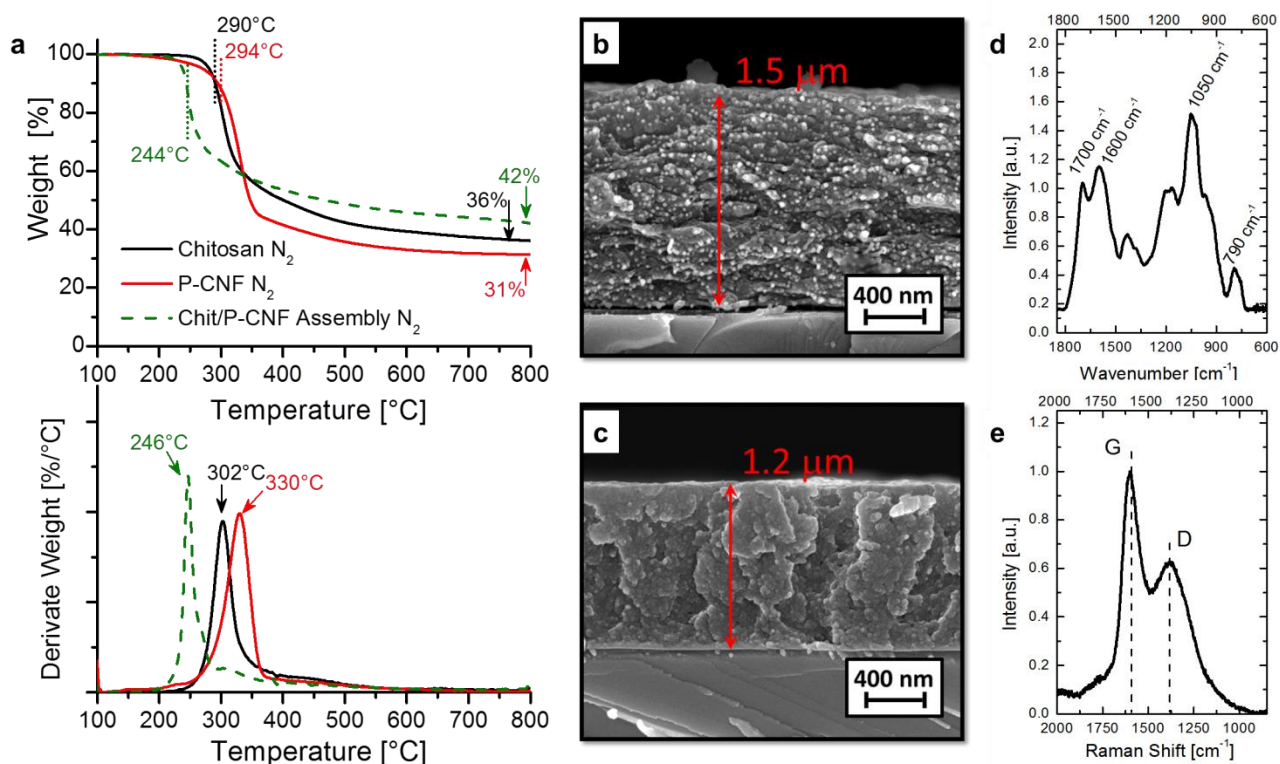
As far as flammability is concerned, upon flame application, the unmodified foam quickly ignites and vigorously burns with flame spreading (1.5 mm/s) to the entire length of the sample. During combustion the foam melts and collapses releasing droplets of burning molten polymer that ignite the dry cotton placed underneath the sample. This behavior, known as melt-dripping, represents one of the most severe safety threat of PU foams as it can easily spread the fire to other ignitable materials leading to dangerous flashover events. Conversely, LbL-coated PU foams showed a completely different burning behavior. Upon ignition a small flame slowly propagates (1.1 mm/s) on the samples leaving a charred residue behind. The melt dripping is completely suppressed and, although the flame spread to the entire length of the sample, at the end of the test it is possible to

325 collect a coherent residue accounting for 10% of the original mass. This points out that the flame
326 self-extinguished before being able to completely consume the PU. From an overall point of view,
327 LbL-treated PU foams show an improved behavior due to the formation of a protective coating that
328 prevents foam collapse and limits the release of combustible volatiles consistently reducing the
329 burning rate. This completely suppresses melt dripping but does not allow for the self-extinguishing
330 of the flame before it spreads to entire length of the specimen. Cone calorimetry tests (Figure 4 b)
331 have been performed using a heat flux of 35 kW/m^2 corresponding to a fire in the developing stages.
332 (Schartel & Hull, 2007) Upon exposure to the heat flux the unmodified PU starts degrading,
333 releasing combustible volatile gases that lead to sample ignition and flaming combustion. During
334 combustion the foam collapses forming a pool of a low viscosity liquid simultaneously reaching the
335 maximum heat release rate (718 k/m^2). (Kramer, Zammarano, Linteris, Gedde, & Gilman, 2010)
336 This behavior has been demonstrated to be very dangerous as it increases the flame spread rate by
337 boosting the combustion rate of other burning items. On the other hand, for the foam coated with 5
338 BL it is possible to observe the formation of a char layer that quickly extends to the entire foam and
339 prevents the structure from collapsing. This partially hinders the foam combustion and results in a
340 reduced pkHRR (- 31%). THR and TSR values remain almost unchanged and within the
341 experimental error. The final residue is slightly increased moving from 6 to 7 % for the uncoated
342 and LbL-coated foams, respectively. Similar to what was observed in the flammability tests, such
343 results can be ascribed to the presence of the coating that acts as a barrier controlling the mass and
344 heat exchange between the gas and condensed phase. This reduces the release rate of the volatiles
345 and subsequently results in a reduction of heat release rate parameters.

346 *3.4 Assembly thermal stability and fire shielding ability on PU foams*

347 From the characterization performed on untreated and LbL-treated foams it is quite apparent that
348 the CH/P-CNF nano-exoskeleton is capable of strongly modifying the foam morphologically and
349 mechanically apart from changing its fire properties. This can be ascribed to the homogeneity and

350 continuous nature of the coating that extends through the entire thickness of the foam covering each
 351 available surface. However, although the change in mechanical properties can be explained by the
 352 strong ionic interactions among the assembled components, there are no studies trying to explain
 353 the improvements in flame retardant properties. Thus, in an effort to further understand the role of
 354 the deposited coating, a detailed study of the thermal stability and structural-chemical evolution of
 355 CH/P-CNF assembly during combustion has been performed. Figure 5 shows the results collected
 356 by TGA under nitrogen atmosphere for neat CH, neat P-CNF and a LbL-assembled CH/P-CNF
 357 model consisting of 150 BL. In addition, the morphological and chemical changes in such LbL
 358 coating deposited on Si wafer following exposure to 35 kW/m² heat flux are displayed.



359

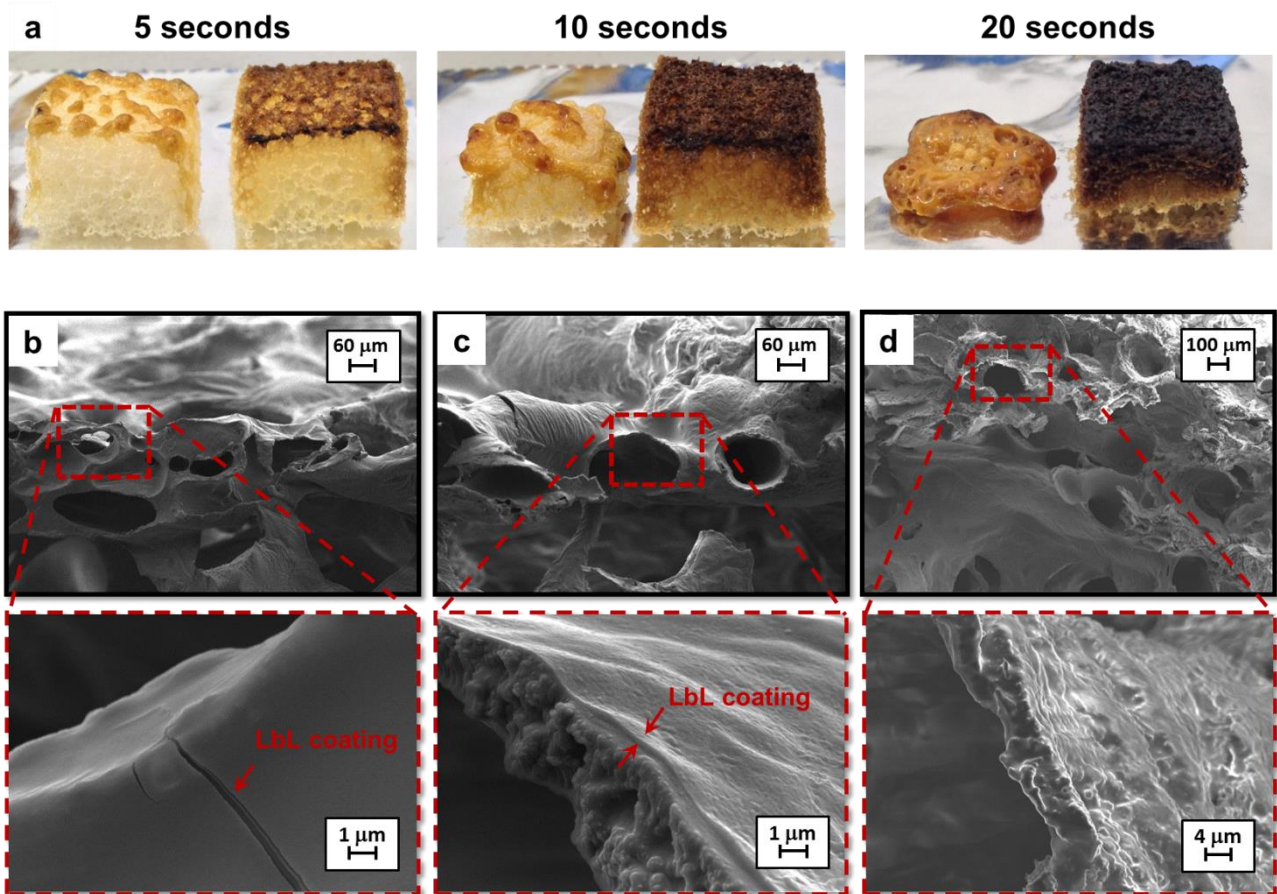
360 **Figure 5.** TG and dTG curves of neat and LbL-assembled components under nitrogen atmosphere
 361 (a), FE-SEM micrographs of the coating cross section before (b) and after (c) exposure to 35
 362 kW/m², IR (d) and Raman (e) spectra of the coating after exposure to 35 kW/m².

363 TGA performed under nitrogen atmosphere simulate the pyrolysis that occurs in the condensed
 364 phase during combustion owing to essentially anaerobic atmosphere under the surface of the

365 burning material. First of all the neat components have been evaluated. Both CH and P-CNF
366 degrade with a well-defined single step that occurs between 250-400°C. As well documented in the
367 literature during this step CH releases H₂O, NH₃, CO, CO₂ and CH₃COOH and forms a
368 carbonaceous residue that subsequently undergoes a slow and continuous modification, with the
369 production of CH₄, towards polyaromatic structures (final residue 36%).(Pawlak & Mucha, 2003)
370 (Corazzari et al., 2015) The P-CNF follows characteristic degradation path of cellulose; however,
371 thanks to the char promoting action of the phosphorylation functionalization, the amount of charred
372 residue produced at the end of the first step and at 800°C is consistently higher (31%) than what
373 normally reported for cellulose or non-phosphorylated CNF. (J. Alongi, Camino, & Malucelli,
374 2013) (Ghanadpour et al., 2015) When the two components are LbL-assembled, the resulting
375 material still shows a single step thermal degradation that is anticipated at 244°C, as reported in
376 Figure 5 a. This can be related to the phosphate groups of P-CNF and, although an earlier
377 degradation may be considered a detrimental effect, it allows the CH/P-CNF coating to promptly
378 react to a temperature raise and produce a thermally stable residue/barrier. Moreover, the resulting
379 thermal stability is unexpectedly higher than that of the pure CH and P-CNF as clearly pointed out
380 by the weight curve that remains above the region associated to any theoretical mixture of non-
381 interacting components. This can be ascribed to the achieved intimate and a stoichiometric
382 assembly of the two components into a material characterized by strong ionic intermolecular
383 interactions. The residue produced after the first step is 70% while the final residue is as high as 42
384 %. The same CH/P-CNF assembly deposited as 150 BL coating on model Si wafer surface, has
385 been exposed to the cone heat flux (the same adopted during the tests on foams) and then imaged
386 with FE-SEM and analyzed by ATR-IR and Raman spectroscopy. FE-SEM observations clearly
387 point out a structural change in the coating that is not destroyed by the heat flux but, as studied by
388 TGA, evolves towards the formation of a charred dense structure with a 25% reduction in thickness.
389 ATR spectroscopy suggests the formation of an aromatic carbonaceous structure (signal at 1600 cm⁻¹
390 ¹ ascribed to aromatic C=C stretching); in addition, the presence of carboxyl groups (1700 cm⁻¹) and

391 only one peak in the 900-700 cm^{-1} region (790 cm^{-1} , ascribed to out of plane C-H vibration in
392 substituted aromatic rings) suggest the formation of aromatic structures with different degrees of
393 substitution. (Soares, Camino, & Levchik, 1995) (Socrates, 2006) A strong signal found at 1050 cm^{-1}
394 can be related to P-O-C or P-N-C bonds indicating the condensed char promoting action of the
395 phosphorylation functionalization. Raman spectroscopy provides information regarding the quality
396 of the produced aromatic char that can be related to its thermal stability. (Carosio & Alongi, 2016a)
397 Two characteristic signals, known as G and D bands, associated to polyaromatic hydrocarbons are
398 clearly visible at 1590 and 1350 cm^{-1} . (Ferrari & Basko, 2013) The presence of the D band,
399 normally associated to defects, corroborates ATR-IR information; however, the fact that this latter
400 band is clearly less intense than the G band indicates the graphitic-like structure of the barrier
401 produced by the thermal degradation of the CH/P-CNF assembly.

402 It is apparent that the favored char forming ability of the CH/P-CNF assembly represents a key-
403 point in the flame retardant activity of the coating. In order to investigate whether this behavior is
404 maintained also when the coating is deposited on PU foams, small (1x1x1 cm^3) species of uncoated
405 and coated foams have been exposed to the cone heat flux and then imaged by FE-SEM. Figure 6
406 summarizes a number of collected snapshots and corresponding micrographs.



407

408 **Figure 6.** Digital images of uncoated and LbL-coated PU foams after exposure to 35 kW/m^2 (a) and
 409 FE-SEM micrographs of LbL-coated PU foam exposed to 35 kW/m^2 for 5 (b), 10 (c) and 20 (d)
 410 seconds.

411 The snapshots clearly point out an extensive char formation for the coated PU foam. This starts
 412 from the top surface and is extended to the entire structure within 20 seconds. During the same
 413 time, the uncoated foam completely melts and collapses. From FE-SEM micrographs it is possible
 414 to observe the presence of a protective char layer on the surface of PU foam. This thin charred layer
 415 is still visible even after 10 seconds of exposure while after 20 seconds it is embedded within the
 416 melting PU. On the basis of the above observations and the coating thermal degradation it is
 417 possible to formulate a mechanism of action for the deposited CH/P-CNF assembly. Upon exposure
 418 to a flame or a heat flux the coating constituents start degrading, building protective layers
 419 characterized by a graphitic like structure. This occurs at low temperatures (around $240 \text{ }^\circ\text{C}$) and

420 produces a compaction in the coating thickness as evidenced by TG and FE-SEM observations on
421 the LbL assembled CH/P-CNF (Figure 5). Such char forming interaction is enhanced by the ionic
422 linkages and the intimate contact established during the LbL assembly which allows for synergistic
423 interactions between the phosphate groups of P-CNF and the protonated amine of CH. In this way
424 the coating can quickly and efficiently evolve towards thermally stable polyaromatic structures that,
425 being located at the interface between the condensed and the gas phase, can exert a flame retardant
426 effect. Indeed, the so produced charred exoskeleton acts as a barrier to heat and volatile release
427 while mechanically sustaining the foam that would otherwise collapse. It is important to highlight
428 the importance of this latter effect as a thin charred layer having a high mechanical stiffness which
429 sustains and supports the foamed structure. These two combined effects allow for the suppression of
430 melt dripping while also strongly affecting volatile release rates thus producing the observed
431 reduction in pkHRR and avHRR values.

432 **4. Conclusions**

433 This paper shows extensive results from layer-by-layer assembled nanostructured thin films based
434 on CH and P-CNF to be used as a flame retardant exoskeleton for PU foams. The build-up of the
435 nanostructured films follows a linear growth regime where the phosphorylated nanocellulose
436 component represents the major fraction of the final assembly. A unique nanostructure comprising
437 phosphorylated nanofibrils embedded within a CH continuous matrix is obtained as demonstrated
438 by field emission scanning electron microscopy. This assembly can be easily deposited on open cell
439 polyurethane foams yielding a submicron exoskeleton capable of covering the complex 3D structure
440 of the foam without altering its open cell nature. Compression test demonstrated that the LbL
441 deposition is capable of improving the mechanical properties of the foam while maintaining its
442 characteristic flexibility. This occurs with only 8% of coating mass added and has been ascribed to
443 the nanostructure of the assembly and the strong ionic interaction occurring at the molecular scale
444 between the assembled CH and P-CNF. From the flame retardancy point of view, coated foams

445 were able to suppress melt dripping during flammability tests and reducing the combustion rate by
446 31% as evaluated by cone calorimetry testing. The mechanism behind the flame retardant effect of
447 the deposited coating has been thoroughly analyzed and correlated with the coating composition
448 and the achieved results. When exposed to a heat flux (or a flame) the coating constituents undergo
449 a favorable degradation pathway that results in the build-up of thermally stable aromatic structures
450 that act as protective barrier towards heat and flammable volatile release. The produced charred
451 barrier also displays impressive mechanical properties as it is capable of mechanically sustaining
452 the foam during combustion preventing its collapse. This is achieved thanks to the unique structure
453 imparted by the layer-by-layer assembly that during thermal degradation favors synergistic rather
454 than simply additive interactions between the two components. This paper allows for a further step
455 towards the efficient use of sustainable resources for the LbL construction of functional flame
456 retardant materials and poses the base for a deeper insight and a better understanding of the
457 structure to properties relationship in FR-LbL assemblies.

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464 References

- 465 Alongi, J., Camino, G., & Malucelli, G. (2013). Heating rate effect on char yield from cotton, poly(ethylene
466 terephthalate) and blend fabrics. *Carbohydr Polym*, 92(2), 1327-1334.
- 467 Alongi, J., Carletto, R. A., Di Blasio, A., Cuttica, F., Carosio, F., Bosco, F., & Malucelli, G. (2013). Intrinsic
468 intumescent-like flame retardant properties of DNA-treated cotton fabrics. *Carbohydr Polym*, 96(1),
469 296-304.
- 470 Alongi, J., Cuttica, F., & Carosio, F. (2016). DNA Coatings from Byproducts: A Panacea for the Flame
471 Retardancy of EVA, PP, ABS, PET, and PA6? *ACS Sustainable Chemistry & Engineering*, 4(6), 3544-
472 3551.

473 Alongi, J., Di Blasio, A., Cuttica, F., Carosio, F., & Malucelli, G. (2014). Bulk or surface treatments of ethylene
474 vinyl acetate copolymers with DNA: Investigation on the flame retardant properties. *European*
475 *Polymer Journal*, 51, 112-119.

476 Aulin, C., Varga, I., Claesson, P. M., Wågberg, L., & Lindström, T. (2008). Buildup of polyelectrolyte
477 multilayers of polyethyleneimine and microfibrillated cellulose studied by in situ dual-polarization
478 interferometry and quartz crystal microbalance with dissipation. *Langmuir*, 24(6), 2509-2518.

479 Cain, A. A., Plummer, M. G. B., Murray, S. E., Bolling, L., Regev, O., & Grunlan, J. C. (2014). Iron-containing,
480 high aspect ratio clay as nanoarmor that imparts substantial thermal/flame protection to
481 polyurethane with a single electrostatically-deposited bilayer. *Journal of Materials Chemistry A*,
482 2(41), 17609-17617.

483 Carosio, F., & Alongi, J. (2016a). Influence of layer by layer coatings containing octapropylammonium
484 polyhedral oligomeric silsesquioxane and ammonium polyphosphate on the thermal stability and
485 flammability of acrylic fabrics. *Journal of Analytical and Applied Pyrolysis*, 119, 114-123.

486 Carosio, F., & Alongi, J. (2016b). Ultra-Fast Layer-by-Layer Approach for Depositing Flame Retardant
487 Coatings on Flexible PU Foams within Seconds. *Acs Applied Materials & Interfaces*, 8(10), 6315-
488 6319.

489 Carosio, F., Alongi, J., & Malucelli, G. (2012). Layer by Layer ammonium polyphosphate-based coatings for
490 flame retardancy of polyester–cotton blends. *Carbohydr Polym*, 88(4), 1460-1469.

491 Carosio, F., Cuttica, F., Di Blasio, A., Alongi, J., & Malucelli, G. (2015). Layer by layer assembly of flame
492 retardant thin films on closed cell PET foams: Efficiency of ammonium polyphosphate versus DNA.
493 *Polymer Degradation and Stability*, 113, 189-196.

494 Carosio, F., Kochumalayil, J., Cuttica, F., Camino, G., & Berglund, L. (2015). Oriented clay nanopaper from
495 biobased components--mechanisms for superior fire protection properties. *ACS Appl Mater*
496 *Interfaces*, 7(10), 5847-5856.

497 Cho, J. H., Vasagar, V., Shanmuganathan, K., Jones, A. R., Nazarenko, S., & Ellison, C. J. (2015). Bioinspired
498 catecholic flame retardant nanocoating for flexible polyurethane foams. *Chemistry of Materials*,
499 27(19), 6784-6790.

500 Corazzari, I., Nisticò, R., Turci, F., Faga, M. G., Franzoso, F., Tabasso, S., & Magnacca, G. (2015). Advanced
501 physico-chemical characterization of chitosan by means of TGA coupled on-line with FTIR and
502 GCMS: Thermal degradation and water adsorption capacity. *Polymer Degradation and Stability*,
503 112, 1-9.

504 Dash, M., Chiellini, F., Ottenbrite, R. M., & Chiellini, E. (2011). Chitosan—A versatile semi-synthetic polymer
505 in biomedical applications. *Progress in Polymer Science*, 36(8), 981-1014.

506 Decher, G. (1997). Fuzzy nanoassemblies: Toward layered polymeric multicomposites. *Science*, 277(5330),
507 1232-1237.

508 Du, X., Zhang, Z., Liu, W., & Deng, Y. (2017). Nanocellulose-based conductive materials and their emerging
509 applications in energy devices-A review. *Nano Energy*.

510 Ferrari, A. C., & Basko, D. M. (2013). Raman spectroscopy as a versatile tool for studying the properties of
511 graphene. *Nat Nano*, 8(4), 235-246.

512 Ghanadpour, M., Carosio, F., Larsson, P. T., & Wågberg, L. (2015). Phosphorylated cellulose nanofibrils: a
513 renewable nanomaterial for the preparation of intrinsically flame-retardant materials.
514 *Biomacromolecules*, 16(10), 3399-3410.

515 Ghanadpour, M., Carosio, F., & Wågberg, L. (2017). Ultrastrong and flame-resistant freestanding films from
516 nanocelluloses, self-assembled using a layer-by-layer approach. *Applied Materials Today*, 9, 229-
517 239.

518 Hammel, S. C., Hoffman, K., Lorenzo, A. M., Chen, A., Phillips, A. L., Butt, C. M., . . . Stapleton, H. M. (2017).
519 Associations between flame retardant applications in furniture foam, house dust levels, and
520 residents' serum levels. *Environment international*, 107, 181-189.

521 Henriksson, M., Berglund, L. A., Isaksson, P., Lindstrom, T., & Nishino, T. (2008). Cellulose nanopaper
522 structures of high toughness. *Biomacromolecules*, 9(6), 1579-1585.

523 Hirschler, M. M. (2008). Polyurethane foam and fire safety. *Polymers for Advanced Technologies*, 19(6),
524 521-529.

- 525 Jorfi, M., & Foster, E. J. (2015). Recent advances in nanocellulose for biomedical applications. *Journal of*
526 *Applied Polymer Science*, 132(14).
- 527 Klemm, D., Kramer, F., Moritz, S., Lindstrom, T., Ankerfors, M., Gray, D., & Dorris, A. (2011). Nanocelluloses:
528 a new family of nature-based materials. *Angew Chem Int Ed Engl*, 50(24), 5438-5466.
- 529 Koklukaya, O., Carosio, F., & Wågberg, L. (2017). Superior Flame-Resistant Cellulose Nanofibril Aerogels
530 Modified with Hybrid Layer-by-Layer Coatings. *Acs Applied Materials & Interfaces*, 9(34), 29082-
531 29092.
- 532 Kramer, R. H., Zammarano, M., Linteris, G. T., Gedde, U. W., & Gilman, J. W. (2010). Heat release and
533 structural collapse of flexible polyurethane foam. *Polymer Degradation and Stability*, 95(6), 1115-
534 1122.
- 535 Lavoine, N., Desloges, I., Dufresne, A., & Bras, J. (2012). Microfibrillated cellulose - its barrier properties and
536 applications in cellulosic materials: a review. *Carbohydr Polym*, 90(2), 735-764.
- 537 Leistner, M., Abu-Odeh, A. A., Rohmer, S. C., & Grunlan, J. C. (2015). Water-based chitosan/melamine
538 polyphosphate multilayer nanocoating that extinguishes fire on polyester-cotton fabric. *Carbohydr*
539 *Polym*, 130, 227-232.
- 540 Li, Y. C., Kim, Y. S., Shields, J., & Davis, R. (2013). Controlling polyurethane foam flammability and
541 mechanical behaviour by tailoring the composition of clay-based multilayer nanocoatings. *Journal*
542 *of Materials Chemistry A*, 1(41), 12987-12997.
- 543 Liu, A., & Berglund, L. A. (2012). Clay nanopaper composites of nacre-like structure based on
544 montmorillonite and cellulose nanofibers—improvements due to chitosan addition. *Carbohydr*
545 *Polym*, 87(1), 53-60.
- 546 Pawlak, A., & Mucha, M. (2003). Thermogravimetric and FTIR studies of chitosan blends. *Thermochemica*
547 *Acta*, 396(1), 153-166.
- 548 Rodahl, M., Höök, F., Krozer, A., Brzezinski, P., & Kasemo, B. (1995). Quartz crystal microbalance setup for
549 frequency and Q-factor measurements in gaseous and liquid environments. *Review of Scientific*
550 *Instruments*, 66(7), 3924-3930.
- 551 Schartel, B., & Hull, T. R. (2007). Development of fire-retarded materials—Interpretation of cone
552 calorimeter data. *Fire and Materials*, 31(5), 327-354.
- 553 Schlenoff, J. B., Ly, H., & Li, M. (1998). Charge and mass balance in polyelectrolyte multilayers. *Journal of*
554 *the American Chemical Society*, 120(30), 7626-7634.
- 555 Soares, S., Camino, G., & Levchik, S. (1995). Comparative-Study of the Thermal-Decomposition of Pure
556 Cellulose and Pulp Paper. *Polymer Degradation and Stability*, 49(2), 275-283.
- 557 Socrates, G. (2006). *Infrared and Raman Characteristic Group Frequencies - Table and Charts*. (third edition
558 ed.): Wiley.
- 559 Stieger, G., Scheringer, M., Ng, C. A., & Hungerbühler, K. (2014). Assessing the persistence, bioaccumulation
560 potential and toxicity of brominated flame retardants: Data availability and quality for 36
561 alternative brominated flame retardants. *Chemosphere*, 116, 118-123.
- 562 Xu, D., Yu, K., & Qian, K. (2017). Effect of tris (1-chloro-2-propyl) phosphate and modified aramid fiber on
563 cellular structure, thermal stability and flammability of rigid polyurethane foams. *Polymer*
564 *Degradation and Stability*, 144, 207-220.

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