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S. Ehsanimehr, Rodolphe Sonnier, P. Najafi, F. Ducos, M. Badawi, et al.. Layer-by-layer polymer deposited fabrics with superior flame retardancy and electrical conductivity. *Reactive and Functional Polymers*, 2022, 173, pp.105221. 10.1016/j.reactfunctpolym.2022.105221 . hal-03590361

HAL Id: hal-03590361

<https://hal.univ-lorraine.fr/hal-03590361>

Submitted on 3 Mar 2022

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Layer-by-layer polymer deposited fabrics with superior flame retardancy and electrical conductivity

S. Ehsanimehr^{a,b}, R. Sonnier^c, P. Najafi^b, F. Ducos^d, M. Badawi^a, K. Formela^e, M.R. Saeb^e, H. Vahabi^{d,*}

^a Université de Lorraine, CNRS, LPCT, F-54000 Nancy, France

^b Department of Organic Chemistry, Faculty of Chemistry, Urmia University, Urmia 57153-165, Iran

^c IMT – Mines Ales, Polymers Hybrids and Composites (PCH), 6 Avenue De Clavières, Alès Cedex F-30319, France

^d Université de Lorraine, CentraleSupélec, LMOPS, F-57000 Metz, France

^e Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland

A B S T R A C T

Smart and multifunctional textiles and fabrics are progressively developing, such that multifunctional fabrics are becoming more widespread. We elaborated herein multi-layered flax fabrics with superior flame retardancy and conductivity, which revealed fireproof feature while keeping conductivity during burning. The flax fabric was reinforced by layer-by-layer (LbL) deposition of sodium polyacrylate (SPA), polyethylenimine (PEI), ammonium polyphosphate (APP), and lastly a composite having poly(aniline-co-melamine) and montmorillonite (MMT) coated the aforementioned layers. The resulting multi-layered fabrics were characterized systematically by Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX) and thermogravimetric analysis (TGA). Flame retardancy of fabrics was conducted on pyrolysis-combustion flow calorimetry (PCFC), and a vertical burning test. TGA test showed a significant increase in the amount of residue of the treated fabrics (37%) against 19% assigned to untreated flax fabrics. Surprisingly, PCFC showed a very low peak of heat release rate (pHRR) of 15 W/g (HRR) for reinforced flax fabrics with respect to 234 W/g assigned to untreated flax fabrics ($\approx -94\%$). In addition, the vertical burning test demonstrated the fireproof character of multi-layered fabrics. The conductivity of coated flax fabric was in the range of $1-8 \times 10^{-7}$ S/cm before burning, which astonishingly survived up to 30 s after burning. This bi-functional flame retardant and conductive fabric enables taking next steps towards development of fireproof conductive materials for advanced technologies.

Keywords:

Natural fiber

Flax fabric

Textile

Flame retardant

Electrical conductivity

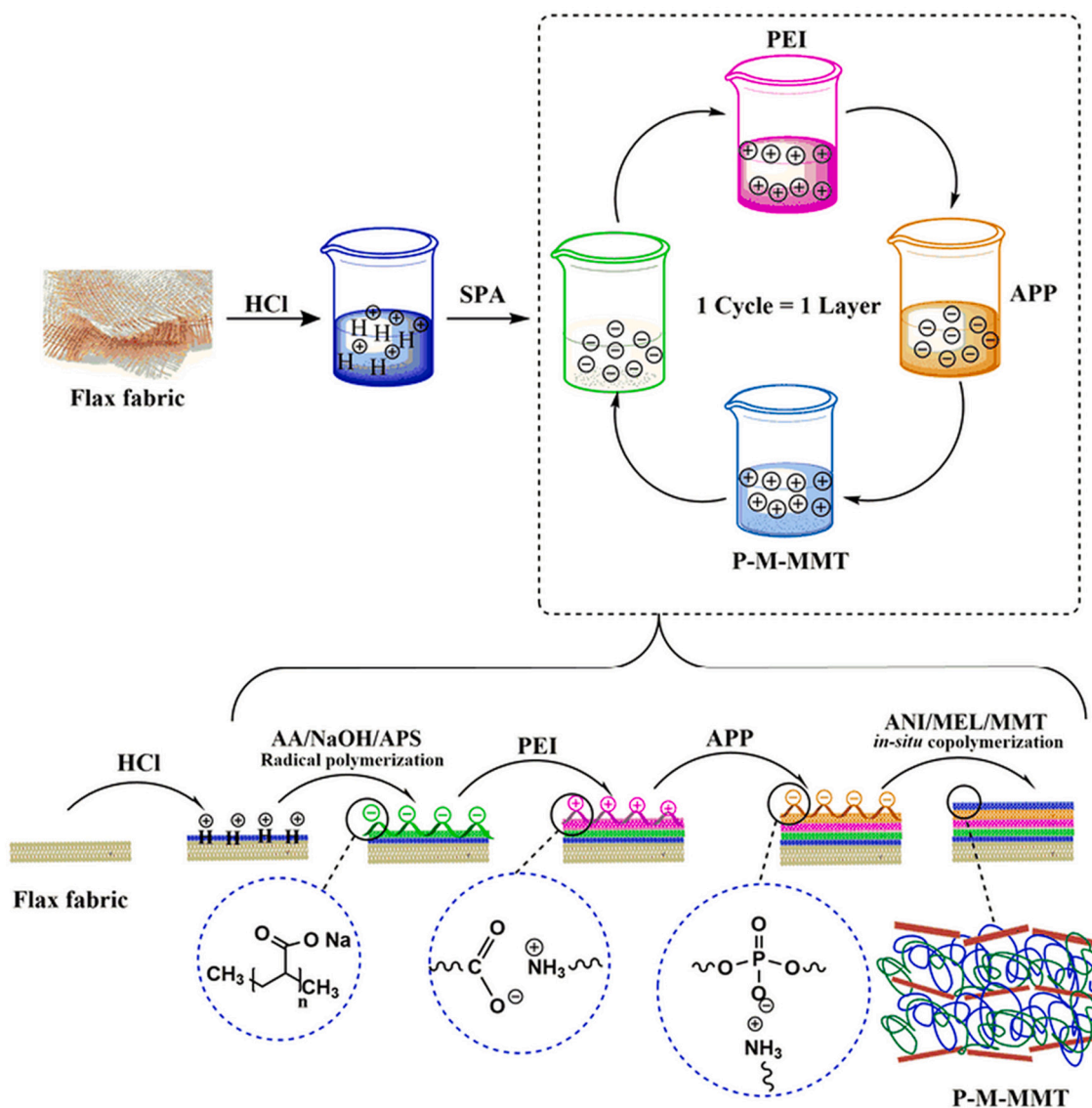
1. Introduction

Textiles industry has always been a dynamic field, resulting from amalgamation of art with science. Over the past century, there has been a global reconsideration in the mission of fabrics, such that smart and multifunctional fabrics have found a privileged position among materials' market [1–3]. Some terms such as “technical textiles” and “smart fabrics” are today established, correspondingly synthetic fibers are replaced by green multi-functional and non-woven ones [4–6]. Conductive textiles and fabrics are an advanced class of smart materials mainly used for the production of heating fabrics (fitness cloths and sport), electromagnetic interference (EMI) shielding, and antistatic materials. Conductive fabrics can be manufactured *in-situ* by surface

grafting of conductive polymers such as polypyrrole, polyaniline, or polyacetylene onto textiles or fabrics; also by applying conductive coatings onto the surface of fabrics by the aid of a binder and a polymer emulsion [6–8]. The markets of conductive textiles and fabrics have dynamited since 2016, particularly by finding new dimensions such as healthcare, medical science, military and defense [9,10]. An almost two-fold jump in the size of market and annual growth rate from 2016 to 2027 highlights the importance of research on conductive fabrics [11]. The military and defense sectors are the major demanders of conductive textiles/fabrics, but still multidimensionality of the used fabrics seems challenging. Some other application realms of conductive polymers include in clothing of astronauts, biological chemistry, energy storage, and protection against weathering [12,13]. Stimuli-responsive fabrics

* Corresponding author.

E-mail address: henri.vahabi@univ-lorraine.fr (H. Vahabi).



Scheme 1. Schematic of fabrication of SPA/PEI/APP/P-M-MMT coatings on the flax fabrics (SPA: sodium polyacrylate, PEI: polyethylenimine, APP: ammonium polyphosphate, P-M-MMT: poly(aniline-co-melamine)/MMT).

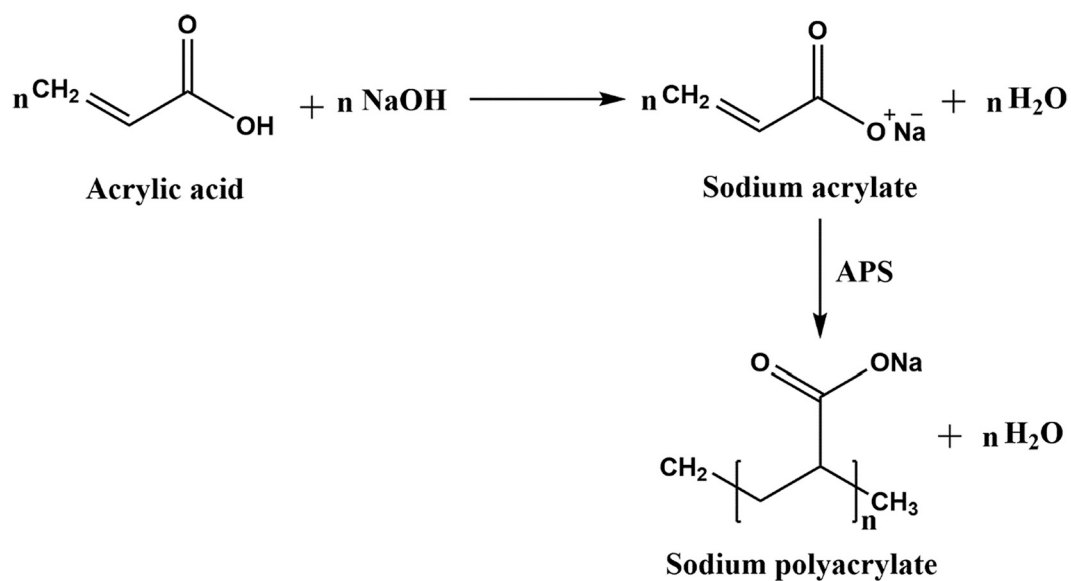
are also developing fast in other fields such as safety clothing and fireproof/self-extinguishing applications [14,15]. Development of multifunctional or smart fabrics has been practiced by materials scientists over the past decades. Fireproof and fire-extinguishing fabrics [16–18] are among advanced materials, which have been in the core of attention in manufacturing fireguards' clothing [19,20]. However, flame-retardant conductive natural fabrics are not easy to achieve. The natural fabrics are highly flammable. Although there have been several reports on development of flame retardant [19,21,22] fabrics and conductive natural fabrics [23–25], there has been no report on development of fireproof or highly flame-retardant conductive natural fabrics in the open literature. In this work, a flame-retardant conductive flax fabric was prepared using layer-by-layer (LbL) [26] deposition method. Using LbL approach, it is possible to coat the surface of flax fabrics by polyethylenimine (PEI), ammonium polyphosphate (APP), and a polyaniline (PANI)-based copolymer consecutively. The deposition on flax fabric was monitored using Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX) and thermogravimetric analysis (TGA). Pyrolysis-combustion flow calorimetry (PCFC), vertical burning and chronoamperometry tests were also used to analyze the flame retardancy and

electrical conductivity of the obtained fabrics, respectively.

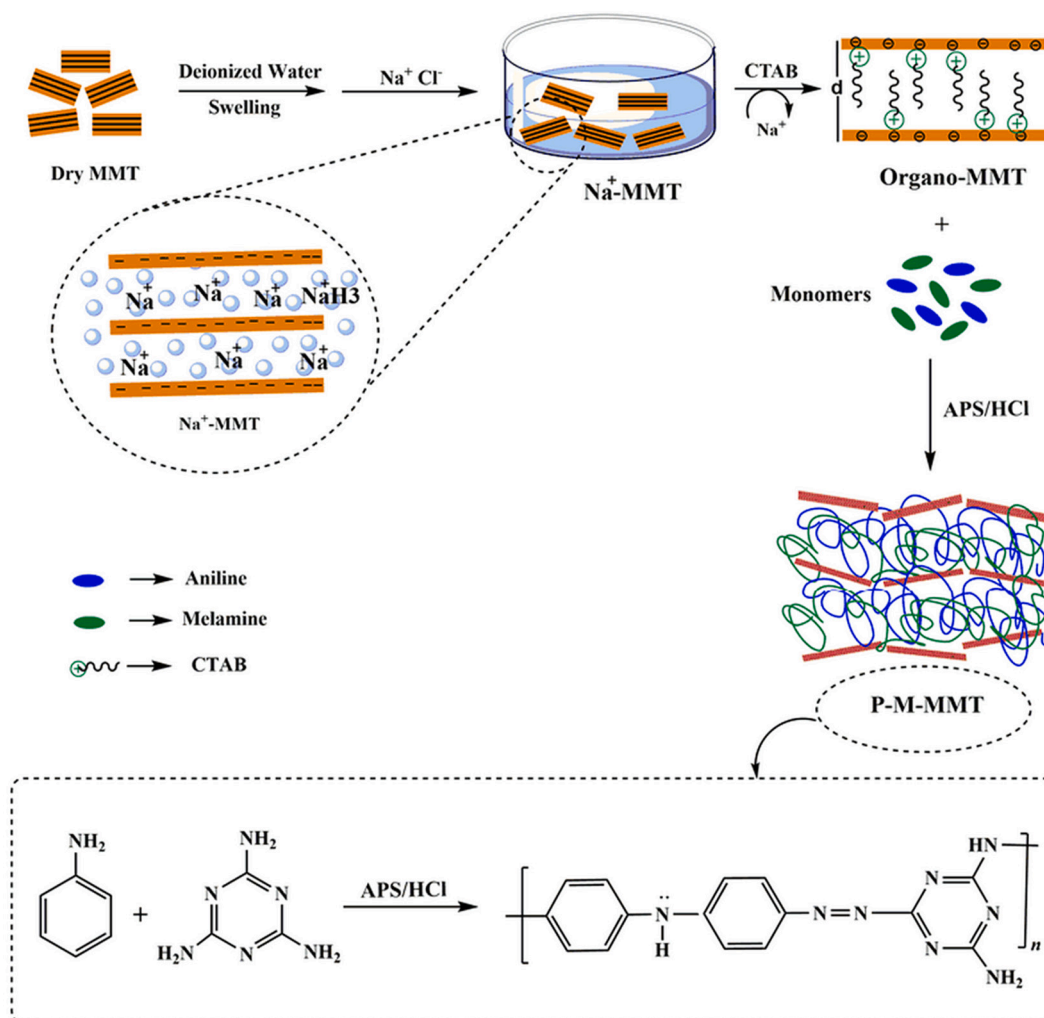
2. Experimental

2.1. Materials

Flax fabrics were provided by Hexcel. Ammonium polyphosphate (APP) (Exolit®AP 423, $[\text{NH}_4\text{PO}_3]_n$ with $n > 1000$, average particle size (D50) = 3 μm , density = 1.9 g/cm^3) was supplied by Clariant, Switzerland. Melamine (MEL) powder ($\text{C}_3\text{H}_6\text{N}_6$) was donated by Urmia Petrochemical Co. (Urmia, Iran). Ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) (APS), polyethylenimine (PEI), acrylic acid (AA), and montmorillonite (MMT) (K10, powder, pH 3–4, surface area: 250 m^2) were all purchased from Sigma-Aldrich. Aniline (Merck Co.) was distilled over zinc dust to obtain a colorless liquid. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) aqueous solutions were prepared using doubly distilled water and all used solvents were purchased by Merck Co. and used without further purification.



Scheme 2. General view of polymerization of sodium polyacrylate conducted in this work.



Scheme 3. In-situ copolymerization of poly(aniline-co-melamine)/MMT (P-M-MMT).

Table 1

Sample codes and formulation prepared and coated on the flax fabrics (1 L: one layer, it refers to on a layer prepared via one cycle of treatment (SPA/PEI/APP/P-M-MMT) coated on the flax fabrics).

Sample code	Formulation
Flax fabric	Untreated flax fabrics
SPA	Flax fabric coated with sodium polyacrylate (SPA)
SPA/PEI	Flax fabric coated with sodium SPA and polyethylenimine (PEI)
SPA/PEI/APP	Flax fabric coated with SPA, PEI and ammonium polyphosphate (APP)
SPA/PEI/APP/P-M-MMT	Flax fabric coated with SPA, PEI, APP and poly(aniline-co-melamine)/MMT (P-M-MMT) composite
1 L/SPA	Flax fabric coated with SPA/PEI/APP/P-M-MMT and a second cycle treatment with SPA
1 L/SPA/PEI	Flax fabric coated with SPA/PEI/APP/P-M-MMT and a second cycle treatment with SPA and PEI
1 L/SPA/PEI/APP	Flax fabric coated with SPA/PEI/APP/P-M-MMT and a second cycle treatment with SPA, PEI and APP
1 L/SPA/PEI/APP/P-M-MMT	Flax fabric coated with SPA/PEI/APP/P-M-MMT and a second cycle treatment with SPA, PEI, APP and P-M-MMT

2.2. Flax fabric treatment

The schematic of LbL coatings on flax fabrics surfaces is illustrated in [Scheme 1](#). The flax fabrics were successively treated with SPA, PEI, APP, and poly(aniline-co-melamine)/MTT (namely P-M-MMT) by a combination of LbL assembly and *in-situ* polymerization. PEI, APP and P-M-MMT were formed in thin layers through secondary interactions such as electrostatic forces, hydrogen bonds and van der Waals forces. The P-M-MMT layer was coated on the surface of fabrics by *in-situ* polymerization. This procedure was repeated two times on flax fabrics ([Scheme 1](#)).

2.3. Preparation of polymer solutions

All polymer solutions with specific weight percentages were prepared in deionized water. The PEI solution (1 wt%) was prepared by dissolving PEI in deionized water and stirring for 2 h to complete dissolution. Then, pH of the solution was set to 7 using 1 M HCl. Moreover, the APP solution (2 wt%) was obtained by adding APP powder in deionized water and sonication for 2 h in an ultrasonic bath to prepare a uniform solution.

2.4. Synthesis and polymerization

Two different methods were combined in preparation of coated fabrics including LbL assembly and polymerization. Prior to the deposition process, the flax fabrics were rinsed with deionized water and acetone, respectively, followed by drying at 70 °C. The flax fabrics was firstly maintained in 0.1 M HCl solution for 15 min to make the fiber surface protonated. The fabric was chemically modified by sodium polyacrylate (SPA) to enhance the compatibility of the flax fabrics with coated layers [27], such that a negatively charged surface was achieved. Briefly, in a two-necked flask (50 mL), NaOH (0.56 g) was dissolved in deionized water (30 mL) followed by addition of AA (1 g) and stirred at room temperature. Then, the flax fabrics were activated by adding the APS (0.23 g) and were added to the aforementioned flask under mild stirring. The radical polymerization of SPA was done at 60 °C under nitrogen atmosphere for 24 h [27], [Scheme 2](#).

The modified fabrics were subsequently washed three times with deionized water and dried in a vacuum oven at 60 °C. Afterwards, the LbL process was conducted by interchangeably immersion of fabrics in cationic PEI solution (1 wt%) and anionic APP suspension solution (2 wt %). After each immersion step, the fabrics were rinsed with deionized water and dried at 60 °C for 30 min. In the last step, a containing poly (aniline-co-melamine)/MMT composite was coated on the surface of fabrics via *in-situ* polymerization. For this purpose, the modified fabrics

Table 2

Details of reactions and fabric treatment (the mass of samples was estimated based on 1 cm² of fabrics).

Sample code	Type of reaction	Reaction temperature and time	Weight (g)
Flax fabric	–	–	0.020
SPA	Radical polymerization	60 °C - 24 h	0.026
SPA/PEI	Layer-by-Layer (LbL)	25 °C - 30 min	0.0313
SPA/PEI/APP	LbL	25 °C - 30 min	0.0353
SPA/PEI/APP/P-M-MMT	<i>In-situ</i> polymerization	0–4 °C - 4 h	0.037
1 L/SPA	Radical polymerization	60 °C - 24 h	0.045
1 L/SPA/PEI	LbL	25 °C - 30 min	0.048
1 L/SPA/PEI/APP	LbL	25 °C - 30 min	0.051
1 L/SPA/PEI/APP/P-M-MMT	<i>In-situ</i> polymerization	0–4 °C - 4 h	0.053

(0.5 g), HCl solution (50 mL, 1 M), melamine (1.34 g), and MMT (20 wt %) were placed into a three-necked flask equipped with an inlet and outlet of the inert gas and kept in an ultrasonic bath ≈30 min. Then, the flask was purged with nitrogen for 20 min until the dissolved oxygen was removed. The APS (4.35 g) was dissolved in deionized water (20 mL) and poured into a funnel. Finally, the aniline (0.5 g) was added to the reaction mixture and cooled down to 0–4 °C in an ice bath. The APS solution was dropped into the reaction mixture for 60 min by holding the reaction temperature at 0–4 °C. Afterwards, the reaction was continued for further 4 h [28]. Then, the flax fabric was washed three times with distilled water and methanol, respectively, and dried in a vacuum oven for 30 min. The reactions performed in the above-mentioned procedures are summarized in [Scheme 3](#). The final product was obtained by an additional LbL process on the surface as described above ([Scheme 1](#)). The samples codes and details of reactions are given in [Tables 1 and 2](#).

2.5. Characterization methods

Fourier-transform infrared (FTIR) spectroscopy was conducted on a Bruker FTIR Alpha apparatus with a resolution of 8 cm^{−1} and 64 scans to characterize flax fabrics and coated flax fabrics. Fiber sections were observed using a scanning electron microscope (FEI Quanta 200). The fibers were cut and imaged vertically. Observations were carried out at a voltage of 12.5 kV under high vacuum and a working distance of 10 mm. Elemental mappings were conducted on an energy dispersive X-ray spectroscopy, EDX, (Oxford INCA Energy system) coupled to SEM. Thermogravimetric analysis (TGA) was conducted on a Setaram Labsys Evo thermogravimetric analyzer to investigate the thermal decomposition of sample in the temperature range of 25–900 °C, at heating rate of 10 °C/min under nitrogen atmosphere. Flammability of the fabrics was analyzed using pyrolysis-combustion flow calorimetry (PCFC, from Fire Testing Technology (FTT), UK) according to method A (anaerobic pyrolysis and complete combustion) [29]. Briefly, few milligrams of samples were pyrolyzed under nitrogen flow at 1 °C/s up to 750 °C. Gases released because of pyrolysis were continuously sent to the combustor at 900 °C in the presence of an excess amount of oxygen (nitrogen/oxygen 80/20). Oxygen consumption measurement allowed for calculating the heat release rate according to the empirical Huggett's relation: 1 kg oxygen consumed corresponds to 1 MJ of energy released (whichever the gases) [30,31]. Heat release rate is plotted *versus* the pyrolysis temperature. The area under the curve corresponds to the total heat release (THR). The sample mass is measured before and at the end of the test to calculate the char yield. Each sample was tested in duplicate. A simple burning test was also performed applying a Bunsen burner on the bottom of the vertical sample for 20 s. The burner moved up after the apparition of flame in order to observe the flame behavior of samples.

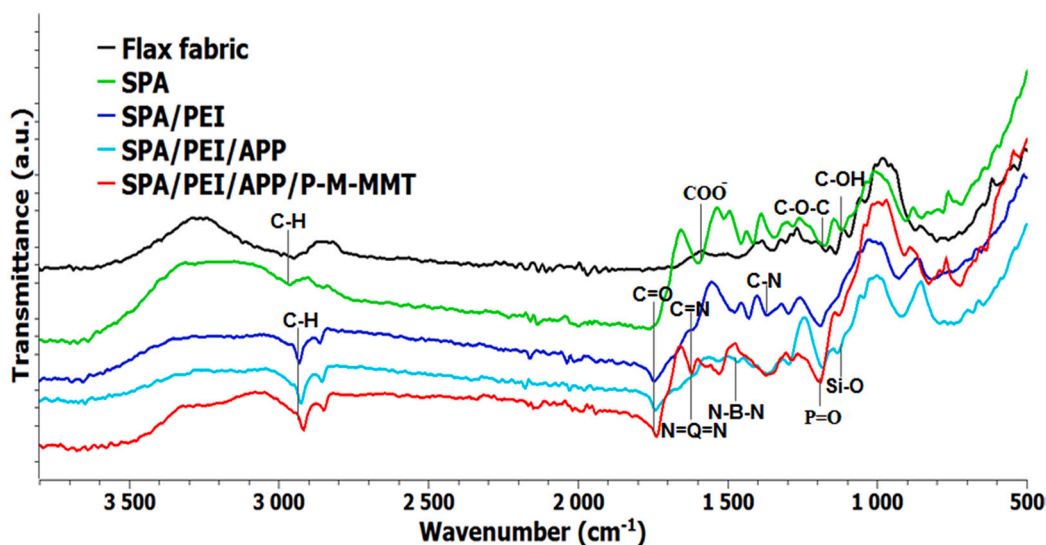


Fig. 1. Fourier-transform infrared (FTIR) spectra of neat flax fabrics and the flax fabric coated with different layers.

Table 3

Band assignments for the FTIR spectra provided from flax fabrics without and with different coatings.

Bond	Vibration type	Wavenumber (cm ⁻¹)
O—H	Stretching	3350–3450
C—H	Stretching	2900
O—H	Bending	1638
C—H ₂ and C—OH	symmetrical deformations	1320–1429
COO ⁻	Asymmetrical Stretching	1590
C—H ₂	Bending	1312–1314
O—H	Bending	1461–1473
C—H	Stretching	1105
C—H	out-of-bending	750
C—O—C, C—C, C—OH	Asymmetrical Stretching	1034–1058
N—H	Bending	1550
N—H ₂	Stretching	3375
C—N	Stretching	1350
P=O	Stretching	1220
C=N	Stretching	1616
N—B—N	Stretching	1480
N=Q=N	Stretching	1600
C—N	Stretching	1285
Si—O	Stretching	1035

The digital videos were recorded, and the selected images were also extracted. The electrical conductivity of the flax fabrics was measured by the chronoamperometry technique with a digital multimeter (ITT Metrix MX 579).

3. Results and discussions

3.1. Chemical structure analysis

FTIR analysis was conducted to evaluate the functional groups presented on the surface of the flax fabrics, Fig. 1 and Table 3. In the case of untreated flax fabrics, the absorption bands between 3350 cm⁻¹ and 3450 cm⁻¹ were related to the OH groups. The band at 2900 cm⁻¹ was related to the C—H stretching of the aliphatic hydrogen groups. The bands in the region 1320–1429 cm⁻¹ were also ascribed to the symmetrical deformations of the CH₂ and C—OH bending vibrations. Moreover, the bending vibration of the OH groups appeared at 1638 cm⁻¹. The bands at 1034–1058 cm⁻¹ were related to C—O—C asymmetrical stretching of C—C, C—OH, C—H ring and side group vibrations [32]. The FTIR spectrum of the flax fabric coated with SPA (SPA) showed peak at 1590 cm⁻¹ corresponding to the COO⁻, while the peak present at

1660 cm⁻¹ was related to -ONa in SPA. The peak at 3409 cm⁻¹ was corresponded to the stretching vibrations of the OH band. For the SPA/PEI sample, the peak at 1550 cm⁻¹ was related to the bending vibrations of the NH₂ group. In addition, the peak at 3375 cm⁻¹ was related to the stretching vibrations of the NH₂ groups, which overlapped with the OH peak and the band at 1350 cm⁻¹ was related to the C—N bond of the amino group of PEI. For the SPA/PEI/APP sample, the peak at 1220 cm⁻¹ was related to stretching vibrations of P=O. For the SPA/PEI/APP/P-M-MMT sample, the band at 1616 cm⁻¹ was related to C=N stretching vibrations in melamine ring. The peak at 1500 cm⁻¹ was related to N—H bending vibration band and the peak at 1196 cm⁻¹ was corresponded to C—N stretching vibration [28]. The peak at 750 cm⁻¹ was related to the out-of-bending vibration of the C—H bond of the benzene ring. The peaks at 1480 cm⁻¹ and 1600 cm⁻¹ were related to stretching vibrations of N—B—N and N=Q=N, respectively (benzenoid (B) and quinoid (Q) structures on polyaniline chains). The peaks at 1105 cm⁻¹ and 1285 cm⁻¹ were also due to the vibration of the C—H and C—N bonds in the benzene ring [28]. Si—O and O—H bonds corresponding to organo-MMT appear at 1035 cm⁻¹ and 3400–3600 cm⁻¹ overlapped with N—H bonds, signature of successful synthesis.

3.2. Morphological analyses

The surface morphologies of the flax fabrics before and after each step of the treatment were investigated by SEM, Fig. 2. The surface of the pure flax fabrics seems smooth and individual fibers can be observed, Fig. 2a. After the treatment, the surface of the fabrics was clearly changed and became rough, Fig. 2b–e. Moreover, the distance between individual fibers were filled with polymers used for modification. This was due to the organic modification, and the secondary interactions such as electrostatic forces, hydrogen bonds and van der Waals forces created between the particles incorporated, polymer layers and flax fibers.

Fig. 3 displays some SEM micrographs of the cross section of the treated flax fabrics and the corresponding element mappings. The section diameter of the unmodified elemental flax fibers is around several dozens of microns and almost no fibers exhibit a lumen. Fibers mainly contain carbon and oxygen (and hydrogen), such that treatments with SPA and SPA/PEI did not change their elemental composition. Phosphorus appears after treatment with APP (SPA/PEI/APP sample), Fig. 3a. In SPA/PEI/APP/P-M-MMT sample, sulfur was additionally observed, because of the ammonium peroxydisulfate used as polymerization initiator. Nitrogen from polyaniline is not clearly detected due to

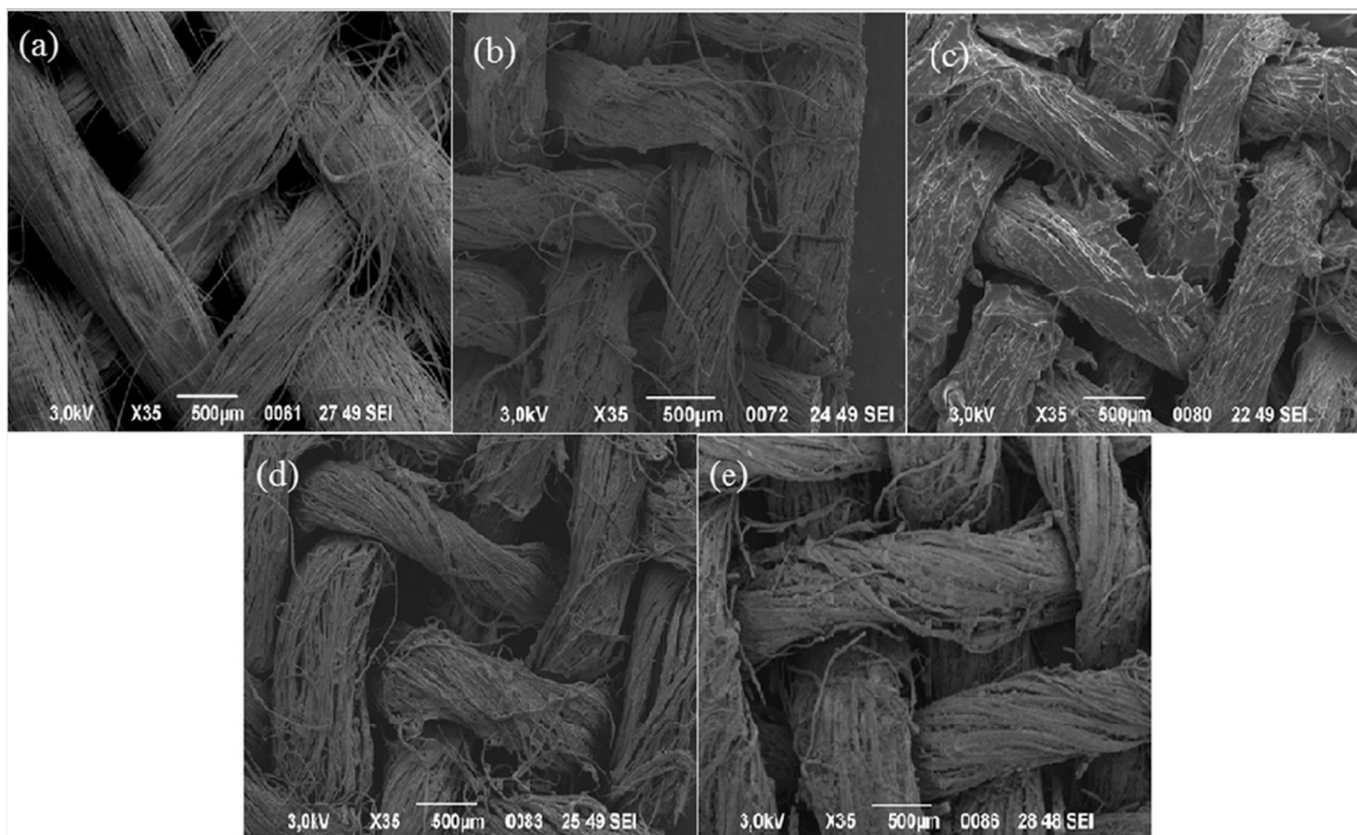


Fig. 2. SEM images of (a) flax fabrics, (b) SPA, (c) SPA/PEI, (d) SPA/PEI/APP, and (e) SPA/PEI/APP/P-M-MMT samples.

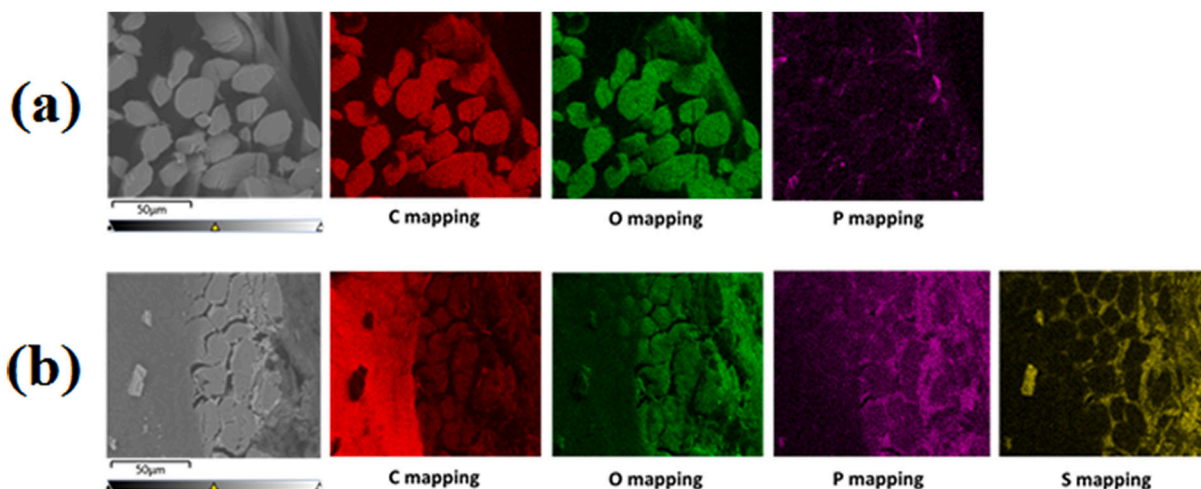


Fig. 3. Elemental mappings of the treated flax fabrics, the first line (a) SPA/PEI/APP, and the second line (b) SPA/PEI/APP/P-M-MMT (C: carbon, O: oxygen, P: phosphorus, S: sulfur).

the overlapping of carbon, nitrogen, and oxygen peaks. Phosphorus and sulfur were observed only at the fibers surface and between elemental fibers, but they were not detected in the bulk of the fibers. This confirms that the components from LbL treatments are formed solely on the surface of fibers and did not penetrate into the bulk.

3.3. Thermal stability analysis

Thermogravimetric analysis (TGA) was performed to evaluate the decomposition behavior of flax fabrics treated with different chemicals.

Fig. 4a and b show the TGA and derivative thermogravimetric (DTG) curves of the studied samples, respectively. The main parameters (T_5 , T_{10} and T_{max} , temperatures corresponding to 5%, 10% and maximum weight loss; as well as residue at 800 °C), were also extracted from these curves and summarized in Table 4. An early and negligible decomposition step was observed for all samples between 50 °C and 120 °C, which can be attributed to the release of water absorbed by fabrics. Afterwards, all samples showed one step of degradation, except for two samples coated with one (SPA/PEI/APP/P-M-MMT sample) and two (1 L/SPA/PEI/APP/P-M-MMT sample) layers of copolymer. The thermal

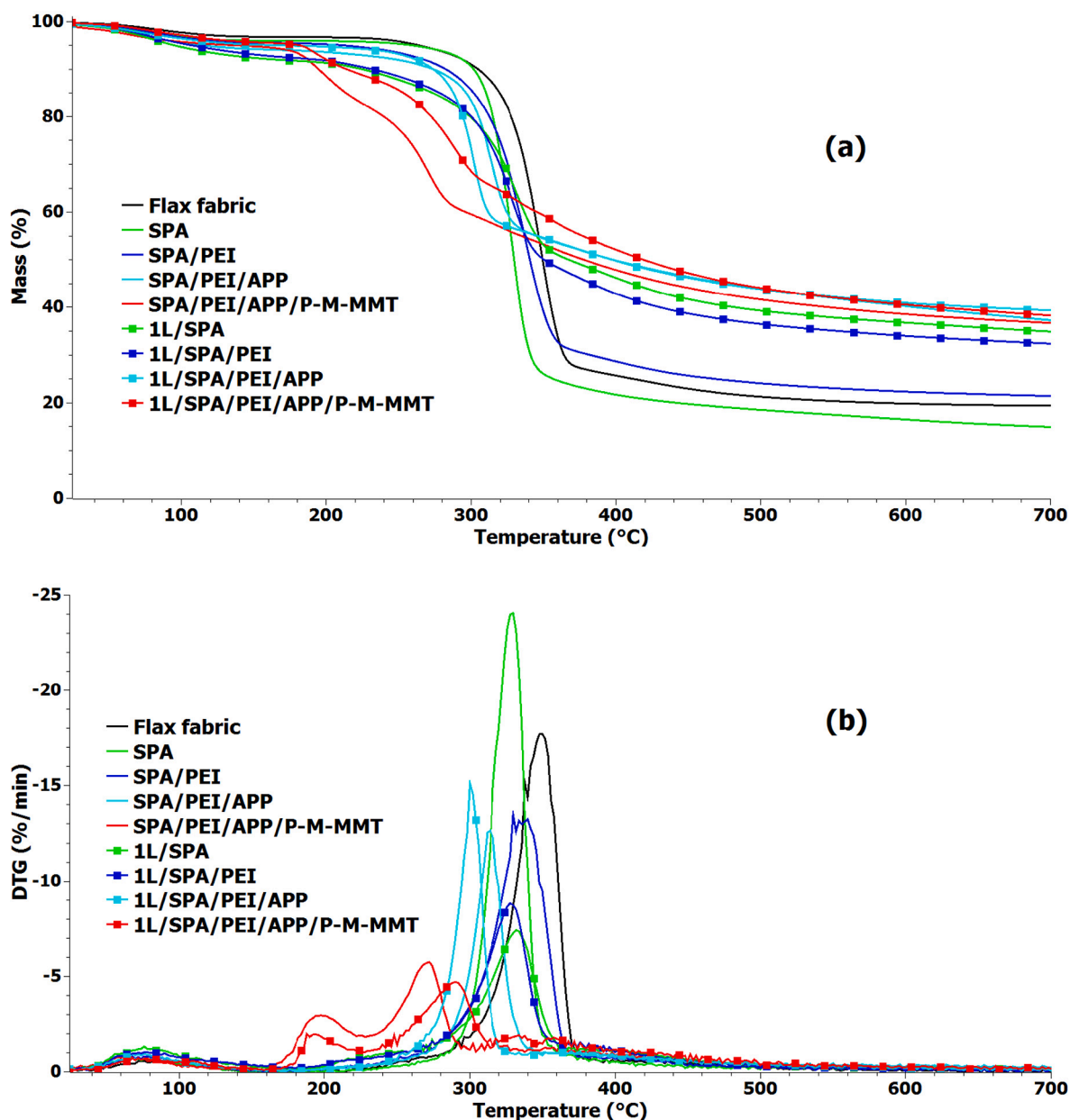


Fig. 4. (a) TGA thermograms of pure flax fabrics and the treated flax fabrics and (b) corresponding DTG curves, under nitrogen 10 °C/min.

Table 4

Summary of the results obtained in TGA tests (T_5 , T_{10} and T_{max} : temperatures at which 5%, 10% and maximum weight loss take place, respectively).

Sample code	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Residue at 800 °C (%)
Flax fabric	264	304	349	19.4
SPA	258	300	329	15.0
SPA/PEI	212	281	334	21.4
SPA/PEI/APP	114	271	314	37.3
SPA/PEI/APP/P-M-MMT	138	193	198–271	36.7
1 L/SPA	96	223	332	35.0
1 L/SPA/PEI	105	229	328	32.3
1 L/SPA/PEI/APP	163	269	299	39.3
1 L/SPA/PEI/APP/P-M-MMT	180	214	192–290	38.2

decomposition of the flax fibers took place at about 220 °C, corresponding to the degradation of cellulose, hemicellulose, and lignin chains [33]. At 500 °C, the aforementioned step of degradation was ended, and the remaining char residue was 19.4%. The value of T_{max} for the flax fabrics was 349 °C. The treatment of flax fabrics with different chemical compounds led to decrease in the T_{max} . For all samples, the first step of decomposition took place before that of flax fabric. However, the thermal stability of all samples increased above 345 °C (above flax fabric), except for SPA sample. It is obvious that the formation of a stable char residue was initiated from 345 °C and the decomposition process was decelerated, leading to increase in the high quantity of the char. Thus, the remaining char residue increased from 19.4% for the flax fabrics to 38.2% for the 1 L/SPA/PEI/APP/P-M-MMT sample. It was also noticed that the first treatment layer (SPA sample) decreased the thermal stability of flax fabrics, and the char residue was even less than that of the untreated flax fabrics. It is perhaps due to the repeated carboxylate groups of this treatment and the release of more CO₂ because of decarboxylation. However, the additional layers significantly improved

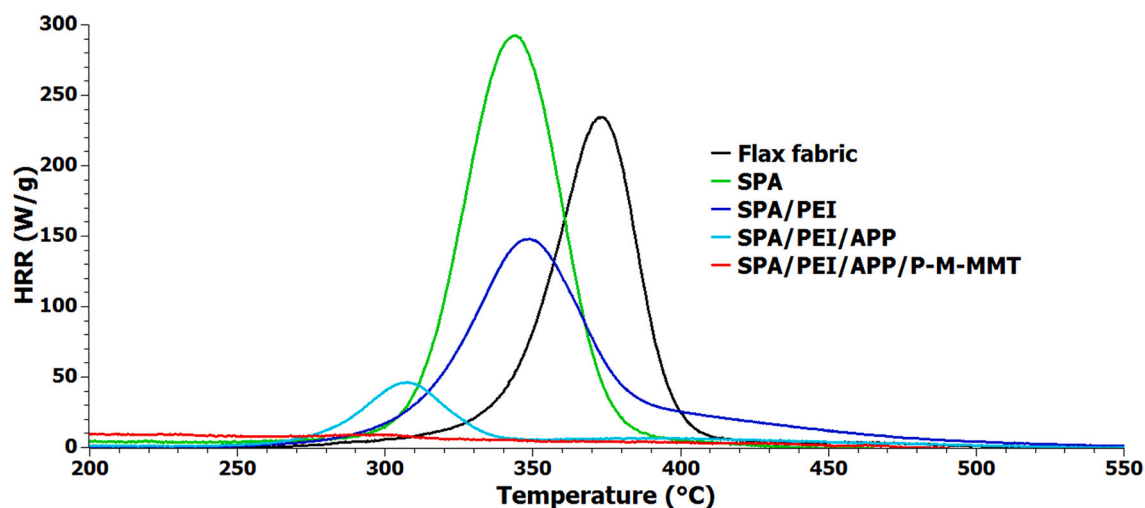


Fig. 5. HRR curves of the treated and untreated flax fabrics (1 layer) obtained in PCFC.

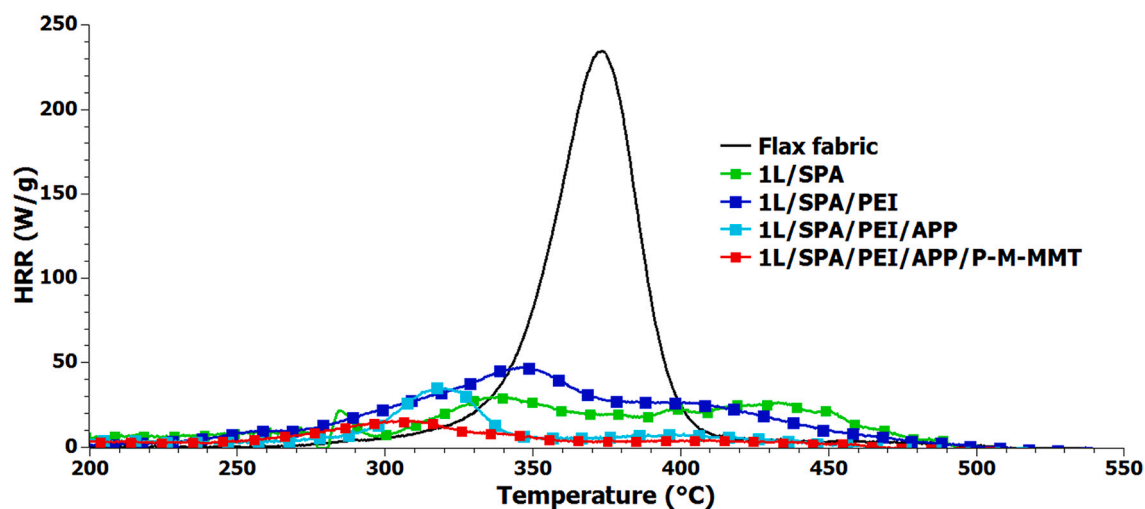


Fig. 6. HRR curves for the treated and untreated flax fabrics (2 layers) obtained in PCFC.

the thermal stability after 345 °C. It is worth to mention that the second layer (cycle) of treatment was useful to increase further the thermal stability when we compare the TGA curves of SPA/PEI and 1 L/SPA/PEI samples or that of SPA/PEI/APP/P-M-MMT and 1 L/SPA/PEI/APP/P-M-MMT samples. The treatment of flax fabric with APP (SPA/PEI/APP and 1 L/SPA/PEI/APP samples) was significantly efficient in increasing the char residue as can be monitored at the end of TGA test. However, these samples were not conductive and an additional treatment with PANI-based copolymer was necessary to give the conductive charter to the flax fabrics. The decomposition pathway of SPA/PEI sample showed that this treatment decreased the thermal stability at the beginning of the test, more than the SPA sample. However, the rate of residue increased because of the presence of nitrogen in PEI, which could participate in formation of a more stable char. The further treatment with APP significantly increased the char residue due to the polymeric character of APP and the presence of phosphorus on its structure, which promoted charring during the decomposition process [34]. The addition of one more layer (P-M-MMT) did not lead to improve further the thermal stability at the beginning of the test. However, the amount of residue was almost unchanged. The presence of last layer may suppress to some extent the charring action of APP. However, this effect was counter-balanced by the high thermal resistance of PANI-based composite deposited at the last layer.

Table 5

Summary results obtained in PCFC tests for the treated and untreated flax fabrics.

	pHRR (W/g)	T _{pHRR} (°C)	THR (kJ/g)	Char yield (%)	Variation in pHRR (%)
Flax fabric	234	373	8.9	0	–
SPA	293	344	12	5	+25
SPA/PEI	147	348	9.5	12	–37
SPA/PEI/APP	46	307	3.2	31	–80
SPA/PEI/APP/ P-M-MMT	–	–	–	28.8	–99
1 L/SPA	30	338	5	32.5	–87
1 L/SPA/PEI	47	347	6.4	30	–80
1 L/SPA/PEI/ APP	34	320	2.5	35	–85
1 L/SPA/PEI/ APP/P-M- MMT	15	303	–	42	–94

3.4. Flammability analysis

All samples were analyzed using PCFC in order to evaluate the effect of each treatment step on the flammability. Figs. 5 and 6 display the heat

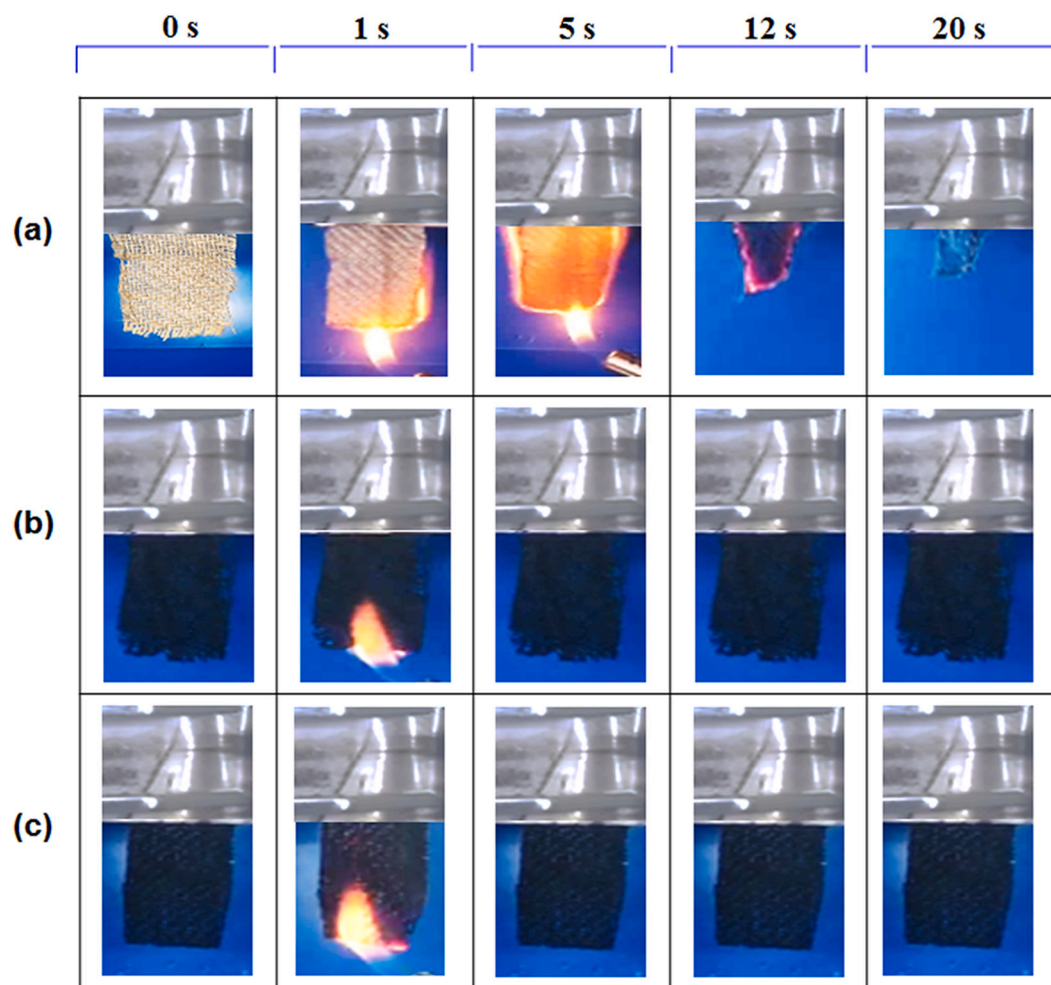


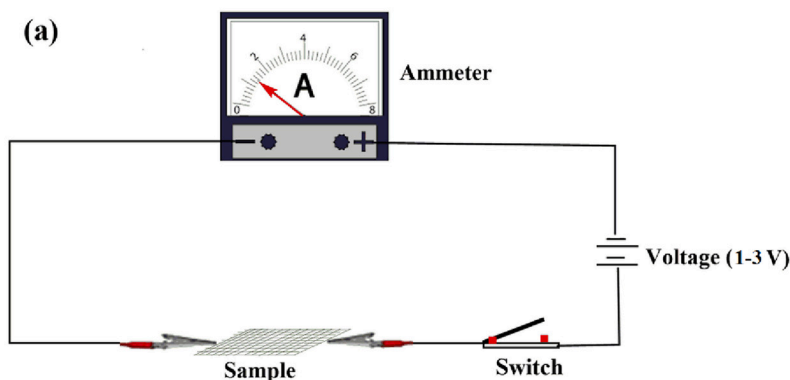
Fig. 7. Digital photos showing the flame behavior of samples, extracted from the video during the vertical flame test (a) flax fabric, (b) SPA/PEI/APP/P-M-MMT, and (c) 1 L/SPA/PEI/APP/P-M-MMT samples (the color of treated fabrics (a and c) is dark-green and remained unchanged after application of flame).

release rate (HRR) curves of samples as a function of temperature. Table 5 summarizes the main results obtained in PCFC, including the peak of HRR (pHRR), temperature at pHRR (T_{pHRR}) and the total heat release (THR). Raw flax fabrics exhibited one pHRR of about 235 W/g at around 373 °C. The THR was 8.9 kJ/g and the amount of residue was negligible. All these data are in good agreement with the previous reports [35]. The modification of the flax fabrics with SPA increased the pHRR to 293 W/g and the THR to 12 kJ/g. The temperature of pHRR was decreased from 373 °C to 344 °C and the char yield was very low (< 5 wt%). It has been reported by Walters and Lyon [36] that the THR of SPA is 12.5 kJ/g with a small residue (6.1 wt%), and pHRR is 165 W/g, which is lower than that of the flax. It may be assumed that acrylic acid catalyzes the decomposition of lignocellulosic fibers leading to a higher pHRR at a lower temperature. SPA/PEI sample showed a lower flammability demonstrated by a single pHRR of 147 W/g at 348 °C. PEI allows for decline in pHRR and THR (9.5 kJ/g), while considerably increases the char yield (12 wt%). This is in good agreement with previous reports [36]. Walters and Lyon [36] measured a low pHRR (121 W/g), and a high char yield (almost 50 wt%) for PEI. Their THR was 11.8 kJ/g, an intermediate value between those of the flax fabrics and SPA sample. The addition of APP meaningfully improved the flame retardancy in SPA/PEI/APP sample. The pHRR decreased to 46 W/g at 307 °C. The lowering of the temperature at pHRR is generally observed in the presence of phosphorus-based flame retardants due to their decomposition into phosphoric acids, leading to an earlier dehydration (and charring) of flax fabrics. The char promotion by APP (char yield 31

wt%) and the lower heat of complete combustion (<5 kJ/g because the char contains a high amount of carbon) lead to a low THR (3.2 kJ/g). The last treatment of the first layer with P-M-MMT in SPA/PEI/APP/P-M-MMT sample allows for further flammability suppression. Its pHRR was very low and hardly visible. Char yield was around 30 wt% and THR was too low to be accurately measured. Therefore, because of its low flammability, this treatment should ensure an excellent fire behavior at bench-scale, according to the works establishing correlations between the PCFC and other fire tests [37]. When a second cycle of the treatment was applied on flax fabrics, a very low HRR was observed. Several peaks can be observed, but lower than 50 W/g. THR was between 5 and 6 kJ/g and char yield was between 30 and 33 wt% for 1 L/SPA and 1 L/SPA/PEI samples, evidencing that a second layer of SPA and PEI tends to increase the flammability compared with SPA/PEI/APP/P-M-MMT sample. 1 L/SPA/PEI/APP and 1 L/SPA/PEI/APP/P-M-MMT samples exhibit lower flammability, but slightly higher than SPA/PEI/APP/P-M-MMT sample. It means that, from a flammability point of view, the second layer is not necessary to achieve a high flame retardancy level.

3.5. Burning behavior analysis

A vertical burning setup was used to compare the flame behavior of samples. Fig. 7 shows the digital images extracted from videos taken during the vertical burning tests. All videos are available as Supporting Information. In the case of flax fabrics, the flame continuously burnt the sample after the ignition to the end of test. The test duration for the



Scheme 4. Electrical conductivity setup applied on flax fabric samples (a), photo of set-up used for measurement of conductivity during the application of flame on conductive flax fabric (b).

Table 6
: Conductivity values for the uncoated and two coated flax fabrics.

Sample code	Voltage (v)	Conductivity (S/cm)	Average conductivity (S/cm)
Flax fabric	1-3	0	0
SPA/PEI/APP/P-M-MMT	1	7.9×10^{-7}	8×10^{-7}
	1.5	7.9×10^{-7}	
	2	8×10^{-7}	
	3	8.2×10^{-7}	
1 L/SPA/PEI/APP/P-M-MMT	1	10×10^{-8}	13.5×10^{-8}
	1.5	12×10^{-8}	
	2	15×10^{-8}	
	3	17×10^{-8}	

untreated flax fabrics took place for 20 s and no residue was remained at the end of the test, signifying highly flammable character of this sample. The same procedure was applied on treated flax fabrics, SPA/PEI/APP/P-M-MMT and 1 L/SPA/PEI/APP/P-M-MMT, but no ignition was tracked at the end of 12 s of application of Bunsen burner. The operation was repeated two times and the treated flax fabrics withstood nonflammable. PCFC and vertical burning tests showed clearly that the treated fabric represented a fireproof character, which is technically better than flame-retardant character. Several treatments were applied on the flax fabrics contributing to this character. From the mechanistic point of view, APP and PEI can significantly contribute to the flame retardancy enhancement by the formation of char residue and the release of nitrogen in form of gases as NH_3 , N_2 , NO_2 to dilute gas phase. In addition, some interactions between the phosphorus and nitrogen may happen leading to reinforce the char residue and; thus, improvement of the flame retardancy *via* barrier effect. However, the presence of a very high resistant temperature composite containing a copolymer of PANI and melamine and MMT seems to be the main reason of fireproof character of the treated flax fabrics.

3.6. Electrical conductivity analysis

The electrical conductivities of the coated and uncoated flax fabrics were measured by the chronoamperometry method at variable voltages in the range of 1 to 3 V, as presented in Scheme 4. The results were expressed with mean \pm SD by repeating the measurements ($n = 4$). The conductivity test was performed according to the Ohm's law of importance, using Eq. (1):

$$R = V/I \quad (1)$$

In this equation, the voltage (V, volts), amps (I, ampere), and the resistance (R, Ohm) are the main parameters of the current-carrying

material. It should be noted that the R is not an intrinsic property of the material, because it is dependent on the shape of the material, while the conductivity (σ) is independent of the physical properties of the material. Therefore, conductivity of the materials can be compared. The relationship between the resistance and the conductivity is correlated according to Eq. (2), (R (Ω), cross-sectional area (A, cm^2), and conductivity (δ , S/cm):

$$\delta = 1/RA \quad (2)$$

Each sample was tested three times, and the average value of conductivity was calculated for the flax fabrics and two samples coated with PANI (SPA/PEI/APP/P-M-MMT and 1 L/SPA/PEI/APP/P-M-MMT) are given in Table 6. The uncoated flax fabric was not conductive, while the electrical conductivity for the SPA/PEI/APP/P-M-MMT and 1 L/SPA/PEI/APP/P-M-MMT samples were 8×10^{-7} S/cm and 13.5×10^{-8} S/cm, respectively. The loss in conductivity after the second cycle of treatment may be explained by the additional organic layers deposited on flax fabric. It was also pointed out that the electrical conductivity can be maintained for 30 s, when a flame was applied on the conductive flax fiber, Fig. 7b (a video of test is available as the Supporting Information).

4. Conclusions

Smart textiles and fabrics are continuously developing for different applications. The natural flax fabrics are also at the core of attention due to their sustainability features. In this work, flame-retardant conductive flax fabrics were prepared via LbL deposition of different chemicals, including APP and a composite containing poly(aniline-co-melamine) and MMT on the flax fabrics. Several techniques were used to characterize the treated flax fabrics including TGA, SEM, FTIR, PCFC, EDX, electrical conductivity and burning tests. It has been proved that the treated flax fabric was fireproof, and the application of the flame could not ignite it. By contrast, the untreated flax fabrics easily ignited and totally burnt. The PCFC analysis also confirmed that the treated fabrics were highly flame retarded with a low pHRR at 15 W/g (about 94% lower than reference sample), such that its contribution to the heat release was indeed negligible. Surprisingly enough, the treated flax fabric preserved its conductivity for 30 s when a flame was exposed to the fabrics. In conclusion, these results showed that the treatment applied in the current study could bring potential for development of smart textiles and fabrics.

CRedit authorship contribution statement

S. Ehsanimehr: Formal analysis, Writing – original draft, Writing – review & editing. **R. Sonnier:** Formal analysis, Investigation. **P. Najafi:**

Investigation, Visualization. **F. Ducos:** Formal analysis. **M. Badawi:** Formal analysis, Investigation. **K. Formela:** Formal analysis, Data curation. **M.R. Saeb:** Validation, Writing – review & editing. **H. Vahabi:** Conceptualization, Methodology, Validation, Data curation, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] Y. Lu, X. Xiao, J. Fu, C. Huan, S. Qi, Y. Zhan, Y. Zhu, G. Xu, Novel smart textile with phase change materials encapsulated core-sheath structure fabricated by coaxial electrospinning, *Chem. Eng. J.* 355 (2019) 532–539.
- [2] J. Wang, J. He, L. Ma, Y. Zhang, L. Shen, S. Xiong, K. Li, M. Qu, Multifunctional conductive cellulose fabric with flexibility, superamphiphobicity and flame-retardancy for all-weather wearable smart electronic textiles and high-temperature warning device, *Chem. Eng. J.* 390 (2020), 124508.
- [3] R. Nazir, D. Parida, J. Borgstätt, S. Lehner, M. Jovic, D. Rentsch, E. Bülbül, A. Huch, S. Altenried, Q. Ren, In-situ phosphine oxide physical networks: a facile strategy to achieve durable flame retardant and antimicrobial treatments of cellulose, *Chem. Eng. J.* 417 (2021), 128028.
- [4] A. Rehman, S. Houshyar, P. Reineck, R. Padhye, X. Wang, Multifunctional smart fabrics through Nanodiamond-polyaniline nanocomposites, *ACS Appl. Polym. Mat.* 2 (11) (2020) 4848–4855.
- [5] S.M. Costa, D.P. Ferreira, A. Ferreira, F. Vaz, R. Fanguero, Multifunctional flax fibres based on the combined effect of silver and zinc oxide (Ag/ZnO) nanostructures, *Nanomaterials* 8 (12) (2018) 1069.
- [6] F. Mokhtari, Z. Cheng, R. Raad, J. Xi, J. Foroughi, Piezofibers to smart textiles: a review on recent advances and future outlook for wearable technology, *J. Mater. Chem. A* 8 (19) (2020) 9496–9522.
- [7] W. Jakup, R.A. Mohamed, G. Rehab, A. Rehan, H. Ali, Preparation and characterization of conductive cellulosic fabric by polymerization of pyrrole, *Mater. Sci. Appl.* 2013 (2013).
- [8] Z. Stempień, T. Rybicki, E. Rybicki, M. Kozanecki, M. Szykowska, In-situ deposition of polyaniline and polypyrrole electroconductive layers on textile surfaces by the reactive ink-jet printing technique, *Synth. Met.* 202 (2015) 49–62.
- [9] L. Van Langenhove, Smart Textiles for Medicine and Healthcare: Materials, Systems and Applications, Elsevier, 2007.
- [10] O. Sahin, O. Kayacan, E.Y. Bulgun, Smart textiles for soldier of the future, *Def. Sci. J.* 55 (2) (2005) 195.
- [11] Military, Healthcare to Boost Conductive Textile Market. <https://www.technicaltextile.net/news/military-healthcare-to-boost-conductive-textile-market-252804.html>, 2019, 2021.
- [12] K. Singha, J. Kumar, P. Pandit, Recent advancements in Wearable & Smart Textiles: an overview, *Mat. Today Proc.* 16 (2019) 1518–1523, <https://doi.org/10.1016/j.matpr.2019.05.334>.
- [13] V. Koncar, Smart Textiles and their Applications, Woodhead Publishing, 2016.
- [14] Y. Zhao, J. Wang, Z. Li, X. Zhang, M. Tian, X. Zhang, X. Liu, L. Qu, S. Zhu, Washable, durable and flame retardant conductive textiles based on reduced graphene oxide modification, *Cellulose* 27 (3) (2020) 1763–1771, <https://doi.org/10.1007/s10570-019-02884-1>.
- [15] R. Cheng, K. Dong, L. Liu, C. Ning, P. Chen, X. Peng, D. Liu, Z.L. Wang, Flame-retardant textile-based triboelectric nanogenerators for fire protection applications, *ACS Nano* 14 (11) (2020) 15853–15863.
- [16] T. Zhang, H. Yan, M. Peng, L. Wang, H. Ding, Z. Fang, Construction of flame retardant nanocoating on ramie fabric via layer-by-layer assembly of carbon nanotube and ammonium polyphosphate, *Nanoscale* 5 (7) (2013) 3013–3021, <https://doi.org/10.1039/C3NR34020A>.
- [17] H. Yan, N. Li, J. Cheng, P. Song, Z. Fang, H. Wang, Fabrication of flame retardant benzoxazine semi-biocomposites reinforced by ramie fabrics with bio-based flame retardant coating, *Polym. Compos.* 39 (S1) (2018) E480–E488, <https://doi.org/10.1002/pc.24617>.
- [18] H. Yan, L. Zhao, Z. Fang, H. Wang, Construction of multilayer coatings for flame retardancy of ramie fabric using layer-by-layer assembly, *J. Appl. Polym. Sci.* 134 (48) (2017) 45556, <https://doi.org/10.1002/app.45556>.
- [19] F.S. Kilinc, Handbook of Fire Resistant Textiles, 2013.
- [20] A.R. Horrocks, 22 - flame resistant textiles for transport applications, in: F.S. Kilinc (Ed.), Handbook of Fire Resistant Textiles, Woodhead Publishing, 2013, pp. 603–622, <https://doi.org/10.1533/9780857098931.4.603>.
- [21] H. Vahabi, F. Laoutid, M. Mehrpouya, M.R. Saeb, P. Dubois, Flame retardant polymer materials: an update and the future for 3D printing developments, *Mater. Sci. Eng. R. Rep.* 144 (2021), 100604.
- [22] T. Zhang, H. Yan, L. Wang, Z. Fang, Controlled formation of self-extinguishing intumescent coating on ramie fabric via layer-by-layer assembly, *Ind. Eng. Chem. Res.* 52 (18) (2013) 6138–6146, <https://doi.org/10.1021/ie3031554>.
- [23] N. Keawpoy, R. Venkatkarthick, P. Wangyao, X. Zhang, R. Liu, J. Qin, Eco-friendly conductive cotton-based textile electrodes using silver-and carbon-coated fabrics for advanced flexible supercapacitors, *Energy Fuel* 34 (7) (2020) 8977–8986.
- [24] S. Varanité, The use of conductive yarns in woven fabric for protection against electrostatic field, *PES* 5 (11) (2010) 13.
- [25] A.-N. Zhang, H.-B. Zhao, J.-B. Cheng, M.-E. Li, S.-L. Li, M. Cao, Y.-Z. Wang, Construction of durable eco-friendly biomass-based flame-retardant coating for cotton fabrics, *Chem. Eng. J.* 410 (2021), 128361.
- [26] X. Qiu, Z. Li, X. Li, Z. Zhang, Flame retardant coatings prepared using layer by layer assembly: a review, *Chem. Eng. J.* 334 (2018) 108–122, <https://doi.org/10.1016/j.cej.2017.09.194>.
- [27] S. Khanlari, M.A. Dubé, Effect of pH on poly (acrylic acid) solution polymerization, *J. Macromol. Sci. A* 52 (8) (2015) 587–592.
- [28] P. Maroufi, P.N. Moghadam, H. Vahabi, New nitrogen-rich flame retardant based on conductive poly (aniline-co-melamine), *React. Funct. Polym.* 150 (2020), 104548.
- [29] R. Sonnier, H. Vahabi, L. Ferry, J.-M. Lopez-Cuesta, Pyrolysis-Combustion Flow Calorimetry: A Powerful Tool to Evaluate the Flame Retardancy Of Polymers, Fire and Polymers VI: New Advances in Flame Retardant Chemistry and Science, 2012, pp. 361–390.
- [30] R. Sonnier, G. Dorez, H. Vahabi, C. Longuet, L. Ferry, FTIR–PCFC coupling: a new method for studying the combustion of polymers, *Combust. Flame* 161 (5) (2014) 1398–1407.
- [31] C. Huggett, Estimation of rate of heat release by means of oxygen consumption measurements, *Fire Mat.* 4 (2) (1980) 61–65.
- [32] M. Wróbel-Kwiatkowska, M. Żuk, J. Szopa, L. Dymińska, M. Maczka, J. Hanuza, Poly-3-hydroxy butyric acid interaction with the transgenic flax fibers: FT-IR and Raman spectra of the composite extracted from a GM flax, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 73 (2) (2009) 286–294.
- [33] D. Zheng, R.-Y. Ding, Z. Lei, Z. Xingqun, Y. Chong-Wen, Thermal properties of flax fiber scoured by different methods, *Therm. Sci.* 19 (3) (2015) 939–945.
- [34] S. Rabe, Y. Chuenban, B. Scharrel, Exploring the modes of action of phosphorus-based flame retardants in polymeric systems, *Materials* 10 (5) (2017) 455.
- [35] R. Hajj, R. El Hage, R. Sonnier, B. Otazaghine, B. Gallard, S. Rouif, M. Nakhil, J.-M. Lopez-Cuesta, Grafting of phosphorus flame retardants on flax fabrics: comparison between two routes, *Polym. Degrad. Stab.* 147 (2018) 25–34, <https://doi.org/10.1016/j.polydegradstab.2017.11.006>.
- [36] R.N. Walters, R.E. Lyon, Molar group contributions to polymer flammability, *J. Appl. Polym. Sci.* 87 (3) (2003) 548–563, <https://doi.org/10.1002/app.11466>.
- [37] R.E. Lyon, N. Safronava, J.G. Quintiere, S.I. Stoliarov, R.N. Walters, S. Crowley, Material properties and fire test results, *Fire Mat.* 38 (2) (2014) 264–278, <https://doi.org/10.1002/fam.2179>.