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Cotton fabric finishing based on phosphate/clay mineral by direct-coating technique and its influence on the thermal stability of the fibers

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A B S T R A C T

Clay minerals are naturally non-combustible materials with potential applications for protection against thermal degradation in textiles. However, their immobilization on the surface of the fabrics is a complicating factor depending on many variables. The application of clay minerals using the technique of finishing by direct-coating seems a viable alternative, which meets the environmental demand for less polluting, fast, simple, and cheap applications. Thus, in the present work, a study about the influence on the thermal stability of cotton fibers, from the textile fabric containing different formulations based on ammonium polyphosphate (APP) and sodium montmorillonite (Na-Mt) was evaluated. The additives were dispersed into a polymeric paste and applied unilaterally on fabric by direct-coating technique. The treated samples showed an improvement in thermal stability and heat release as a function of the Na-Mt/APP ratio loaded into the fabric. A reduction of the heat release rate (pHRR) around 51.6% and an increase of the carbonaceous residue at 800 °C was observed. The study of the thermal stability of the treated cotton fabric using the techniques of PCFC and TGA, with the aid of an experimental planning allowed the understanding of the interaction and synergy phenomena between the components of the formulation applied via direct-coating.

Keywords:

Cotton fabric
Montmorillonite
Thermal degradation
Thermal stability
Direct-coating
Textile finishing

1. Introduction

The use of textile materials in everyday life goes far beyond clothing and household items, its incorporation into the composition of different objects and environments offers comfort, beauty, and functionality to users. However, textile materials, especially those of cellulosic origin, are highly flammable and, therefore, the increasing use of textiles in the different services sectors needs materials with specific characteristics [1–4]. Cotton fibers consist of approximately 94% cellulose and present a Limiting Oxygen Index (LOI) of 18.4, which makes cotton fabrics highly flammable [5]. For these reasons, the search for effective solutions that meet the usability requirements of the fabrics and guarantee a process of obtaining and sustainable application has been growing worldwide.

Studies on improving the resistance to thermal degradation of cotton fibers reported in the literature most often propose chemical methods of modifying the fibers in an aqueous reaction medium, with additives that could generate wastewater containing high loads of polluting

compounds [2,6–8]. According to Liang, Neisius and Gaan [9] the flame retardant coating finishing technique for textiles can be considered one of the most convenient, economical, and efficient alternatives to protect the substrate from burning. For Li et al. [10], and Pan et al. [11], the flame resistance of different polymer matrices has been improved by the incorporation of nano-based coatings of lamellar silicates, such as montmorillonite. Direct-coating is a textile finishing process for fabrics used to obtain very specific end-use products like protective clothing, furniture covering, upholstery, mattresses, tarpaulins, thermal insulation fabrics/electric, waterproof fabrics, tablecloths, car seat, opaque fabrics like blackout curtains, among others. However, it is a technique that also offers the alternative of functional applications for the simple, cheap, and fast manufacture of products with greater added value, such as technical textiles [12]. The direct-coating technique is the simplest process of coating fabrics, often known as “floating knife” or “knife over air”. During application the fabric is stretched until it forms a uniform surface without tensioning in the orthogonal directions, as the fabric is passed through the knife, the polymeric resin is spread evenly over the

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surface (uni/bilaterally) [12]. The amount of resin applied depends directly on the dispersion/solution concentration (solids content), resin temperature, distance between knife and fabric, porosity and structure of the fabric, type of fiber, and application speed [12].

Various research works addressed solutions to the flammability of textile fibers proposing alternative methods and the use of different materials to obtain the thermal protection of fabrics and textile fibers [1, 2,4,5,13,14]. The use of clay minerals has been increasing due to their physical-chemical and naturally non-combustible characteristics [15–18]. Among all clay minerals, montmorillonite is the most explored due to its physical-chemical and structural properties (swelling, adsorption, plasticity, ion exchange, colloid formation, rheology, among others) [19]. These properties make it a multifunctional material suitable for the controlled release of compounds, soil remediation, adsorption of contaminants from wastewater and atmosphere, supports for electrochemical catalysts, polymer additives, among others [19]. Montmorillonite crystalline structure is formed by layered silicates and is composed of a central layer formed by alumina octahedrons ($\text{AlO}_4(\text{OH})_2$) surrounded by two layers formed of silica tetrahedrons (SiO_4), with a sandwich-like structure [19] and a chemical formula that can be written as $\text{Al}_{2-x}\text{Mg}_x(\text{Si}_4\text{O}_{10})(\text{OH})_2(\text{Na}_x \cdot n\text{H}_2\text{O})$.

Different studies evaluated the influence of the addition of Mt onto thermal behavior of polymers and textiles. Kiliaris and Papaspyrides [16] and Laoutid et al. [15] reported in their work that low amounts (~10% w/w) of clay minerals added to polymers can contribute to the thermal protection of these materials. Rehan et al. [20] developed a nanocomposite based on chitosan (Cs), silver (Ag) nanoparticles (NPs) and sodium montmorillonite (Na-Mt) for application in cotton fabrics, and showed that the incorporation of additives led to a multifunctionality fabric. Besides Mt, kaolinite has been evaluated in order to improve flame retardancy of textiles and polymers in general. Jose et al. [21] coated a lightweight wool fabric with pure nano-kaolinite (~370 nm) using the exhaustion method (high temperature) followed by a superficial homogenization by a pad-batch process. The authors observed an increase in the LOI from 25 (raw fabric) to 33 (fabric containing 2% kaolinite m/m), with no improvement in the LOI for values above 2% of kaolinite. Batistella et al. [22] evaluated the influence of the ultrafine kaolinite dispersion within a polyamide-6 (PA6) matrix. The authors studied the thermal and mechanical properties of the composite and observed that the PA6 flammability is altered by the presence of the clay mineral; they also reported an increase in thermal stability and a significant reduction in the heat release rate (HRR) of the material. Abou El-Kheir et al. [23] studied a formulation based on nano-kaolinite (<10–100 nm) and sodium polyacrylate applied to viscose fabric using the pad-dry cure method. The research showed an increase in the tensile strength of the fabric according to the proportions of nano-kaolinite in the formulation, and the finishing showed bactericidal and/or inhibitory activity for *Bacillus cereus*, *Candida albicans*, and *Staphylococcus aureus*.

Generally speaking, the accumulation of clay minerals on the surface of a material, at least to a certain extent, acts as a protective layer that limits the transfer of heat and oxygen from the gas phase to the material, limiting the pyrolysis process and the mass transfer of fuels into the surrounding atmosphere. In general, the addition of clay minerals in polymers can reduce the peak heat release (pHRR) of the material; however, it does not decrease the total heat released (THR). It means that all combustible material can be consumed, however, slower than in the absence of clay mineral [17]. Moreover, in most cases, the use of clay minerals alone is not enough to achieve the required level of flame retardancy, sometimes requiring the combination of clay minerals and a phosphorus-based compound due to the synergy effects between the materials [4,13,24,25].

The analysis of fabrics containing flame retardant finishing is one of the most critical steps in the process of developing textile products for this purpose, but crucial for the success of applied technology [26,27]. Industries and laboratories commonly use LOI (limiting oxygen index),

thermogravimetry (TGA), and vertical fabric burning test (ASTM D 6413) to analyze this finishing. The LOI test determines the ability/chance of a material to ignite, but it is not able to offer other critical information related to the combustion of the textile material, such as the peak heat release rate (pHRR). Another difficulty to perform the LOI test for synthetic fiber fabrics is related to the plastic melting of the sample [26–28]. Although the vertical burning of the fabric provides a quick and visual presentation of the burning, it is a non-quantitative method and sometimes is carried out in poorly controlled conditions [26]. In vertical burning, it is also difficult to perform the test for samples of thermoplastic fabrics and mixtures, being another limitation of the technique [26,27]. Another laboratory technique is the cone calorimetry, according to Yang et al. [26], and Nazaré, Kandola and Horrocks [29], this technique is very effective in determining the rate of heat release from plastic materials; however, it encounters experimental difficulties in the evaluation of fabrics for two reasons, the thickness of textile samples (weight: g/m^2), and the difficult samples preparation in a standardized way. Nazaré, Kandola and Horrocks [29] successfully report the use of an assembly technique to evaluate fabrics in cone calorimetry; however, the repeatability for daily tests is still low.

The most important parameter in determining the fire hazard of a material is the maximum speed that the continuous heating of that material has in generating more heat (pHRR), and any of the most applied techniques mentioned above provide this information [26,27,30]. Pyrolysis combustion flow calorimetry (PCFC) also known as micro-scale combustion calorimetry (MCC) is a relatively recent technique that uses samples in the order of milligrams (~10 mg), with the capacity to measure the heat release capacity (HRC), heat release rate (HRR), peak heat release (pHRR), total heat released (THR) and temperature at peak heat release (TpHRR) [27,30]. Yang et al. [26] found that the MCC technique can differentiate changes in the flammability of materials. The authors [31,32] proposed a mathematical expression to predict LOI values using data obtained from the PCFC analysis [26,30]. Yang and coworkers performed the LOI and PCFC test for 15 samples of different textile fibers (natural, regenerated and synthetic); the calculated results were tabulated together with the practical results of LOI, and an excellent agreement was observed between the values found. The method proposed by Yang et al. [26] was successfully validated and the authors concluded that the PCFC can be used as a reliable analytical technique in assessing the flammability of textile materials [26,27,30].

For the reasons mentioned above, the present work proposes a study on the influence on the thermal stability of cotton fibers from the textile fabric containing different formulations (m/v) based on APP and montmorillonite dispersed in a polymeric paste, applied unilaterally on fabric by direct-coating technique. The thermal stability of treated cotton fabrics was evaluated by PCFC and TGA, with the aid of an experimental planning that allowed the understanding of the interaction and synergy phenomena between the components of the formulation applied via direct-coating.

2. Experimental

2.1. Materials

Woven fabric (100% cotton) with a weight of 209 g/m^2 was purchased from a local market (Santa Catarina, Brazil) and used as a substrate. Sodium montmorillonite (Na-Mt) under the trade name Cloisite®Na⁺ (Southern Clay Products, USA) was supplied by Buntech Tecnologia de Insumos (Brazil). Ammonium polyphosphate (APP) under the name Charmax NH 1000 (10–12 m.u.; P: 31–32%; N: 14–15%) was provided by Polymer Additives Group (Focus Química, Brazil), and used as received. Poly (vinyl alcohol) stabilized vinyl acetate-ethylene copolymer dispersion under the trade name VINNAPAS®323 or V323 (Wacker Chemical Corporation, USA) was used as a binder between the cotton fabric and the Na-Mt/APP. All chemical reagents were used without further treatment.

2.2. Experimental procedure

Five formulations (F1 to F5) were prepared with different mixing ratios of % Na-Mt and % APP, according to the experimental design. For each formulation, 200 mL of coating-paste was prepared, and all components of the mixture were calculated in the m/v ratio as shown in Table 1. The Na-Mt was delaminated in distilled water under vigorous stirring using an Ultra-Turrax homogenizer for 3 min at 15,000 rpm, and a viscous slurry was obtained. Then, APP was added to the Na-Mt delaminated suspension, at this point the mixture becomes a very viscous paste. Finally, 10% (m/v) of V323 was added to the mixture of each formulation and homogenized under constant stirring (10,000 rpm). The final mixture was referred to as coating-paste. Cotton fabric was treated with the coating-paste using a roller-knife coating equipment attached to a lab stenter Mathis LTE-S (Fig. 1). The thickness of coatings (30 μ m) was controlled by digital micrometers located on the two sides of the roller-knife. Subsequently, the samples were dried in a lab stenter for 6 min at 110 °C (1100 m³/h airflow). Na-Mt and APP add-on values coated on the treated samples were calculated according to their concentration on the coating-paste of each treatment. Table 1 shows the Na-Mt and APP add-on values in the treated samples on a dry basis.

2.3. Characterization

2.3.1. Thermogravimetric and differential thermal analysis (TGA/DTG)

To evaluate the thermal behavior of treated (samples containing the coating-paste) and untreated (samples without coating-paste) cotton fabric, it was used a Jupiter STA-449 F3 (Netzsch, Germany) thermogravimetric analyzer. Approximately 10 mg of sample was inserted into an alumina pan, and the mass loss as a function of the temperature was measured from room temperature to 800 °C, under nitrogen flow (20 mL/min) at a heating rate of 10 °C/min.

2.3.2. Thermal analysis by pyrolysis combustion flow calorimetry (PCFC)

The flammability of treated and untreated cotton fabric was studied using an FTT Micro-calorimeter (Fire Testing Technology Ltd., UK) equipment. Samples were heated from room temperature to 750 °C, with a heating rate of 1 °C/s, under nitrogen atmosphere in the pyrolysis chamber. In the second stage, the gases from the degradation are oxidized in a combustion chamber at a constant temperature (900 °C), with a flow rate of N₂ and O₂ at 80 and 20 cc/min respectively. The heat release rate (HRR) was monitored by the oxygen depletion method. All tests were repeated in triplicate and mean values are reported. Char

Table 1

Na-Mt and APP concentration (%) used in the coating paste formulation and real percentage into the cotton fabric samples after finishing.

Sample	Concentration in the coating paste		FR content coated on cotton fabric		
	Na-Mt (%)	APP (%)	Na-Mt (%)	APP (%)	Na-Mt/APP ratio
F1	2	1	1.78 \pm 0.13 ^a	0.89 \pm 0.06 ^a	2
F2	4	1	6.30 \pm 0.34 ^b	1.58 \pm 0.08 ^b	4
F3	2	3	0.97 \pm 0.15 ^c	1.45 \pm 0.22 ^b	0.66
F4	4	3	2.73 \pm 0.25 ^d	2.05 \pm 0.19 ^c	1.33
F5	3	2	3.48 \pm 0.20 ^e	2.32 \pm 0.13 ^d	1.5

Note: Results are reported as mean \pm the standard deviation (SD) of 10 independent determinations. The lower-case letters (a, b, c, d and e) are the results of Tukey's range test, used to find means that are significantly different from each other, means followed by the same lower-case letters in a column do not differ significantly to the level of 5% probability (p-value > 0.05).

yield was determined by the mass difference of each sample before and after the flammability tests.

2.3.3. Scanning Electron microscopy analysis (SEM)

The morphologies of char residue of treated and untreated cotton fabric after PCFC analysis were examined using a TM3030 (Hitachi) Scanning Electron Microscope, with an accelerating voltage of 4 kV and a current of 10 μ A.

2.3.4. Energy-Dispersive spectroscopy analysis (EDS)

Elementary composition present in the PCFC residues of treated and untreated samples, was obtained by Energy-Dispersive Spectroscopy using a Swift ED3000 instrument attached to the SEM equipment.

2.3.5. Tensile strength analysis

The tensile strength tests of all samples were adapted from ABNT NBR ISO 13934–1: 2016 [33] standard. To perform the tests a Texturimeter equipment model TA-HD Plus from Stable Micro Systems with a 50 kgf (0.5 kN) load cell was used. The rupture force was recorded for six samples and mean values are reported.

2.3.6. Statistical analysis

The statistical analysis was processed using the statistical software package Statistica 7.0 (StatSoft Inc, USA). Differences between individual means were tested using the Tukey test (significance level considered equal to 0.05). To evaluate the coating composition in the thermal stability of cotton fabric, a two-level 2² full factorial design (FFD) with center points was used. The effect of Na-Mt and APP concentration and their interaction on the THR was analyzed and the experimental data were fitted to a first-order model (Equation 1). Analysis of variance (ANOVA) and the lack-of-fit test were used to check the adequacy of the statistical model proposed.

$$Y_i = C_0 + \sum C_i X_i + \sum C_{ij} X_i X_j \quad (1)$$

Y_i is the experimental response, X_i and X_j are the independent variables (factors) and C_0 , C_i , and C_{ij} are the intercept, linear and interaction regression coefficients, respectively.

3. Results and discussion

3.1. Thermogravimetric and differential thermal analysis (TGA/DTG)

Fig. 2a plots the DTG (I), and TGA (II) curves, and complete results are shown in Table 2. The thermogram of untreated fabric reveals a small initial mass loss of around 6%, below 110 °C, which can be attributed to cellulose dehydration (release of free and/or structural water). The main degradation stage occurs between 300 and 375 °C, with a rapid loss of mass of about 75% at 364 °C. In this phase, most pyrolysis products are released, for example, L-glucose, alcohols, esters, CO, and H₂O. Above 400 °C a second degradation step occurs with a residue of about 15% at 450 °C [26,34]. The addition of Mt/APP leads to a thermal destabilization of cotton with a lower onset and peak degradation temperatures. The decrease of thermal stability of cotton with ammonium polyphosphates is reported in the literature and can be explained by the phosphorylation of cotton and the formation of aromatic compounds [35–39]. It should be noted that an anticipation of the degradation can be advantageous for cotton since it can promote the formation of a thermally stable char at lower temperatures, limiting the formation of combustible products [1,40]. Cotton fabric leads to a residue of about 8% at 800 °C. The addition of Na-Mt and APP leads to a different behavior as a function of additives ratio [41]. F1 formulation leads to a decrease in residue whereas F2, F3, and F4 lead to a significant increase and F5 to a small increase. As expected, formulations containing higher amounts of APP or Na-Mt lead to the highest residues.

Comparing the results of experimental and theoretical mass loss

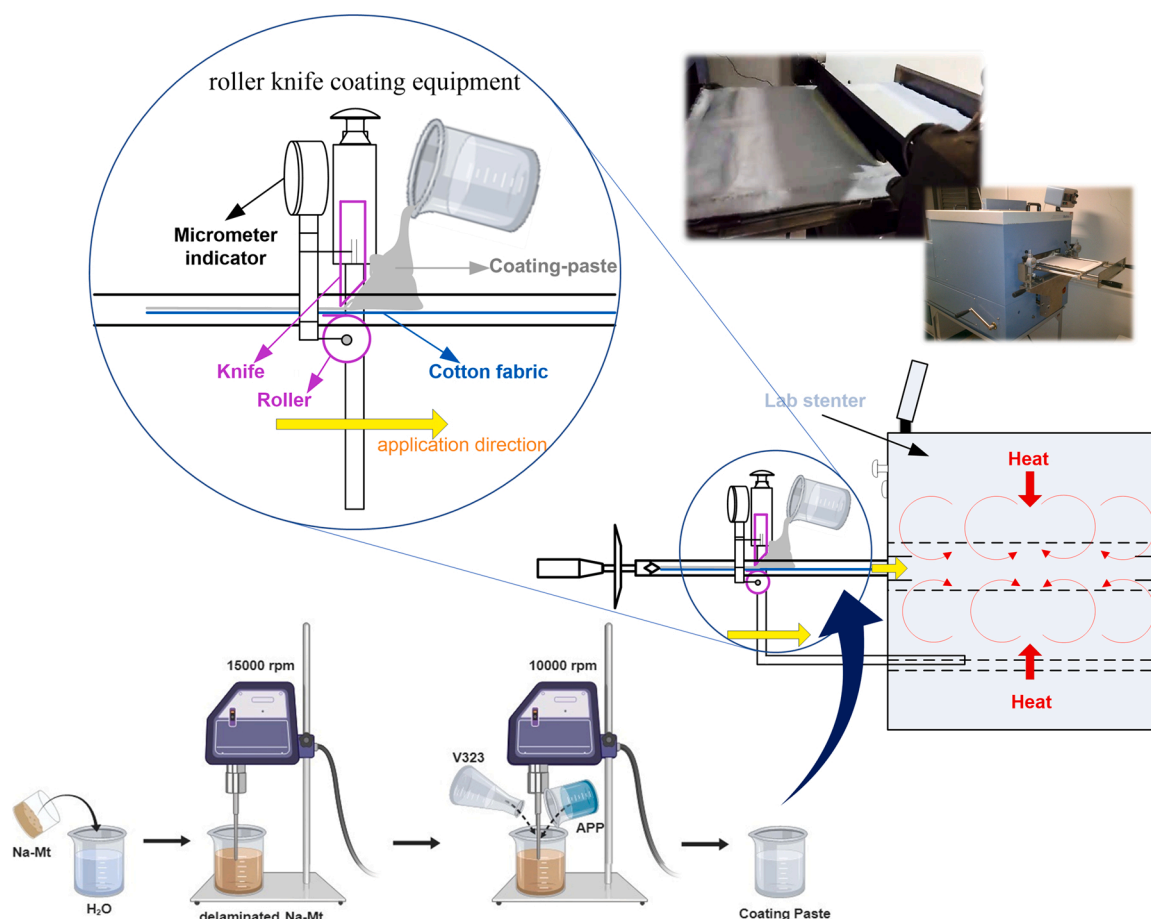


Fig. 1. Schematic representation of the coating paste preparation procedure and its application on cotton fabric by direct-coating technique using a roller-knife coating equipment attached to a lab stenter.

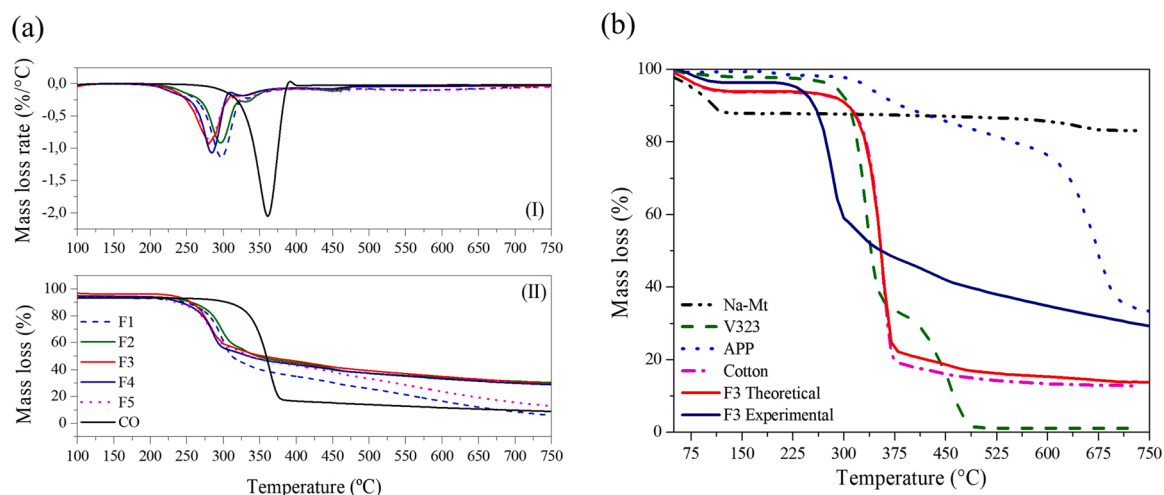


Fig. 2. (a) - DTG (I) and TGA (II) curves of untreated and treated cotton fabric samples under nitrogen flow (20 mL/min) at a heating rate of 10 °C/min (●● F1; ≡ F2; ≡ F3; ≡ F4; ●● F5; ≡ CO). (b) - Theoretical and experimental TGA curves of F3 sample and its components under nitrogen flow (20 mL/min) at a heating rate of 10 °C/min (●● Na-Mt; ●● V323; ●● APP; ●● Cotton; ≡ F3 Theoretical curve; ≡ F3 Experimental curve).

curves shown in Fig. 2b, it can be observed a lower onset degradation temperature as well as the higher residue of experimental results, indicating the formation of a more stable residue. The Na-Mt thermogram shows a first mass loss at 110 °C which can be attributed to the adsorbed water on the clay mineral. Then, a slight mass loss between 600 and 700 °C can be observed, possibly due to its dehydroxylation or to inorganic

contaminants that may eventually be present [42,43]. Results of V323 crosslinker (dried prior to analysis) show two degradation steps, the first starts between 330 and 375 °C due to the formation of acetic acid with a mass loss of about 70%, and the second between 375 and 480 °C to the degradation of olefinic part (C=C and C-H bonds) [44]. The APP curve shows two degradation steps between 300 and 700 °C, the first can be

Table 2

Thermogravimetric data of treated and untreated cotton fabric under nitrogen flow (20 mL/min) at a heating rate of 10 °C/min.

Sample	$T_{\text{onset}10\%}$ (°C)	T_{max} (°C)	Residue at T_{max} (%)	Residue at 800 °C (%)
CO	305	364	39.41	8.17
F1	247	300	61.43	4.02
F2	256	297	70.71	29.71
F3	256	279	74.55	27.94
F4	241	286	67.11	27.75
F5	236	282	70.65	10.57

related to the elimination of NH_3 and water, with a maximum degradation temperature of 332 °C. The second step can be associated with the formation and release of phosphoric, polyphosphoric and metaphosphoric acids at a maximum temperature of 670 °C [45,46].

3.2. PCFC thermal analysis

TGA analysis allows a better understanding of thermal decomposition of the treated and untreated samples, whereas the Pyrolysis Combustion Flow Calorimeter (PCFC) is a good tool to evaluate the material's ability to ignite and the amount of heat released by the one during its thermal degradation [47–49]. The HRR curves of all samples are shown in Fig. 3 and complete results are reported in Table 3.

Cotton fabric degrades in a single step with a pHRR of about 207 W/g at 386 °C with a 3% residue [50,51]. As observed in TGA, the addition of Na-Mt and APP leads to a thermal destabilization of cotton with a decrease in pHRR temperature depending on APP content and Na-Mt/APP ratio. The pHRR of the treated samples varied from 100.1 ± 0.67 W/g to 145.9 ± 1.45 W/g, and the highest reduction in pHRR was observed in the F3 sample. For F1 and F2 samples, which have the lowest APP content, only two peaks were observed whereas F3, F4 and F5 samples an intermediate peak at about 293, 297, and 301 °C respectively, was observed.

The peak between 375 and 475 °C can be assigned to the crosslinking agent V323 present in the samples. An intermediate peak between 290 and 350 °C could be attributed to APP on account of the NH_3 and phosphate compounds release [45,46]. As observed in TGA, the coating-paste incorporation leads to a decrease in degradation temperature, possibly due to the phosphorous compounds that may catalyze the dehydration of cellulose followed by the formation of a carbonaceous barrier [4]. Some studies explain the decrease of the pHRR caused by silica/phosphorous compounds system by a physical barrier to pyrolysis

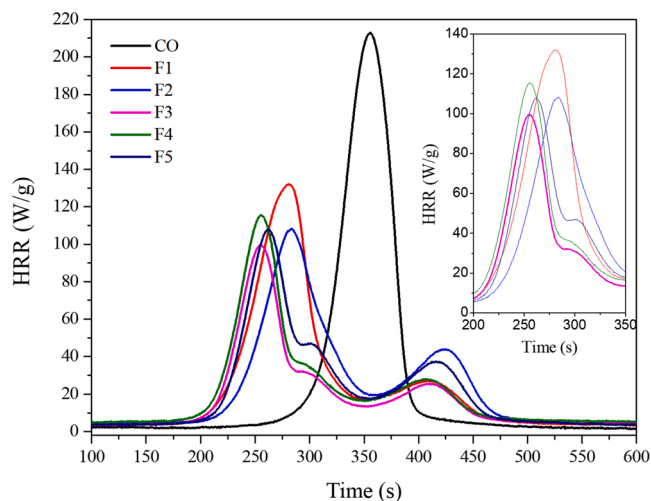


Fig. 3. Heat release rate (HRR, W/g) curves for untreated and treated cotton fabric samples by PCFC, (—) CO; (—) F1; (—) F2; (—) F3; (—) F4; (—) F5).

Table 3

Combustion data obtained from PCFC test.

Sample	THR (kJ/g)	pHRR(W/ g)	T_{pHRR} (°C)	Reduction in pHRR (%)	Char yield (%)
CO	10.4 ± 0.6	207.0 ± 6.1	385.9 ± 2.2	—	3.06 ± 1.81
F1	9.9 ± 0.1	145.9 ± 1.45	324.8 ± 0.9	29.52 ± 0.70	21.50 ± 2.08
F2	9.4 ± 0.1	107.7 ± 0.57	325.7 ± 1.0	47.98 ± 0.27	25.77 ± 3.82
F3	6.7 ± 0.2	100.1 ± 0.67	301.5 ± 0.5	51.65 ± 0.33	23.88 ± 1.79
F4	7.7 ± 0.1	111.1 ± 4.45	299.7 ± 1.5	46.32 ± 2.15	33.87 ± 0.54
F5	8.2 ± 0.5	105.9 ± 1.90	305.0 ± 0.4	48.84 ± 0.92	34.39 ± 1.98

gases and heat transfer, retarding the combustion process [16,52–55]. Vaia et al. [56] further propose that clay minerals may have a catalytic role in the char formation reaction, which occurs due to the acidic sites formed in the silicates by the degradation of the organic treatment, especially in the case of Na-Mt which has high ion exchange capacity and can be activated by protonation [56–59]. A mechanism proposed by Zhu et al. [60] further suggests that paramagnetic metals possibly present in Na-Mt may act as radical trappers, such as iron and aluminum, capable of inhibiting degradation. Such phenomena could partially explain the results obtained by the combination of APP and Na-Mt. In order to evaluate possible synergism between APP and Na-Mt, EDS analysis was carried out in PCFC residue.

3.3. Characterization of PCFC residue

The atomic percentages of the different elements present in the char residues of the treated cotton fabric samples were summarized in Table 4. The existence of the phosphorus element in the residue indicates that phosphorylation reactions between cellulose and the APP occur during combustion. F3 sample, which presented the lowest HRR, showed a decrease in the weight percentage of oxygen in the char residue, while the weight percentages of carbon and phosphorus increased. F1 sample has the APP and clay mineral lowest content and intermediate Na-Mt/APP ratio, but the sample has almost the same percentage of phosphorus retention as F2, F3, and F4 samples. F2 sample has the greatest APP content, but this does not lead to an increase in char content. All of these observations indicate that some interaction effects between Na-Mt and APP occur, which leads to a reduction in pHRR, THR, and an increase in char yield as a function of the Na-Mt/APP ratio. This result shows that the correct proportion of APP and Na-Mt could lead to some synergy effect by the trapping phosphorous resulting in an improved surface barrier and an improved char yield. Micrographs of PCFC residues are shown in Fig. 4. It can be observed that part of the cellulose fibers was partially preserved after burning and presents a fragmented and unstructured characteristic. It is possible to note a complete structure loss of F1 whereas F3 seems to maintain the fiber structure.

Table 4

Atomic percentage of different elements presents on PCFC residue of treated cotton fabric samples determined by EDS analysis.

Sample	C (%)	N (%)	O (%)	P (%)	% of initial P remaining in the residue
F1	66.725	1.450	27.000	0.617	14.9
F2	57.091	3.541	32.548	0.676	11.1
F3	83.518	—	13.982	0.917	15.1
F4	71.841	3.231	21.633	1.062	17.5
F5	56.246	—	35.913	1.917	28.3

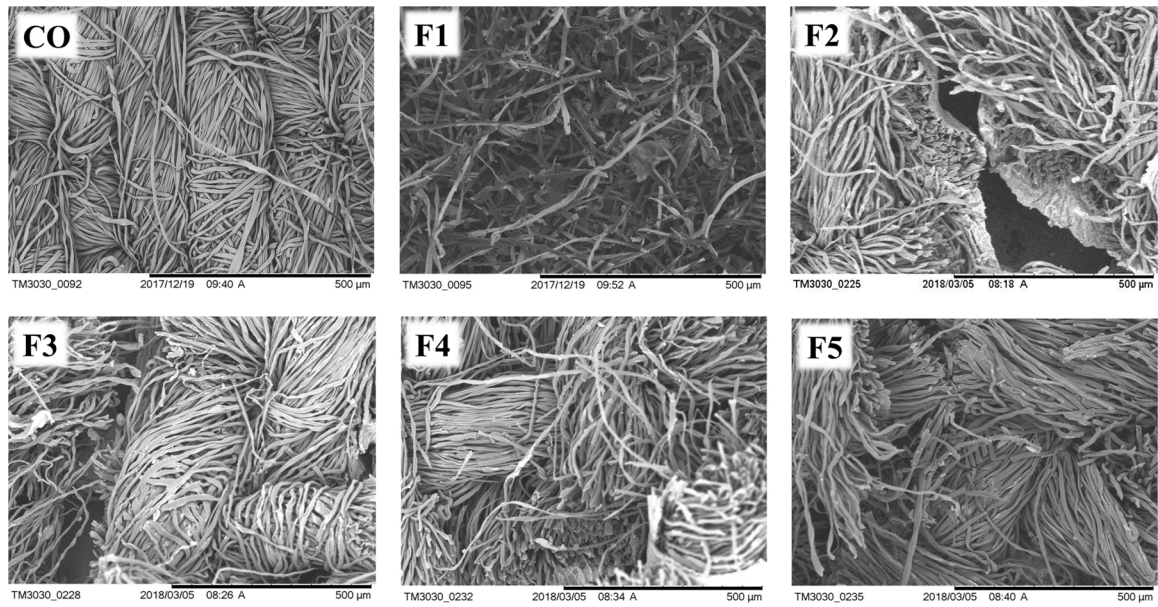


Fig. 4. SEM micrographs of the treated samples residues obtained from PCFC analysis (CO: untreated fabric; F1: Na-Mt/APP = 2; F2: Na-Mt/APP = 4; F3: Na-Mt/APP = 0.66; F4: Na-Mt/APP = 1.33; F5: Na-Mt/APP = 1.5). The image of F1 concerning the others is the one with the most degradation, while F3 appears to have a greater preservation of the fibers after the PCFC test, in agreement with the data obtained in the other analyses.

3.4. Statistical analysis

The main and interaction effects of APP and Na-Mt content in the coating-paste were analyzed and the analysis of variance (ANOVA), at 95% confidence level, is shown in Table 5. The APP content (B) had the greatest significant effect (p -value < 0.05) on total heat release, followed by the two-way interaction effect of Na-Mt and APP (A-B). The effect of Na-Mt and APP concentration and their interaction on the THR were analyzed and the experimental data were fitted to a first-order model (Equation 1). This effect can be better observed by analyzing THR data of treated samples containing 2% Na-Mt (F1 and F3 samples). Increasing APP concentration in the coating composition formulation from 1% to 3%, THR values decreased from 9.9 ± 0.1 kJ/g to 6.7 ± 0.2 kJ/g (reduction of 33%).

Despite the main effect of Na-Mt had no significant effect (p -value > 0.05) on heat released from the cotton fabric; this effect should not be excluded from the analysis, since there is an interaction effect between Na-Mt and APP. The synergetic effect of clay minerals and conventional phosphorus-based flame retardants has been reported in the literature [61–63]. According to Alongi et al. [13], there is an inherent tendency to the intense formation of a carbonaceous residue when flaming combustion occurs in a polysaccharide material containing phosphorus and nitrogen compounds. In this case, the phosphorylation of the cellulose fibers led to the formation of thermally stable char, capable of acting as a barrier that limits the transfer of heat, combustion gases and oxygen between the gas phase and the fibers, which explains the phenomenon studied as in the schematic representation of Fig. 7. The results of THR can be satisfactorily described by the linear regression model given by

Table 5

. Analysis of variance (ANOVA) for total heat release (THR, W/g). SS = sum of square. df = degree of freedom. MS = mean square.

Source	SS	df	MS	F-value	p-value
Na-Mt (A)	0.12500	1	0.12500	1.0504	0.352413
APP (B)	12.00500	1	12.00500	100.8824	0.000167
A-B	1.28000	1	1.28000	10.7563	0.021962
Lack-of-fit	0.14400	1	0.14400	1.2101	0.321436
Pure error	0.59500	5	0.11900		
Total SS	14.14900	9			

Equation (1), as confirmed by ANOVA and lack-of-fit test. The coefficient of determination (R^2) was found to be 0.9477, ensuring a good adjustment of the statistical model to experimental data. The contour plot for THR (Fig. 5) generated with Eq. (2), clearly illustrates the influence of the APP and Na-Mt in the coating-paste formulation on THR.

Irrespective of Na-Mt concentration in the coating-paste, a reduction in the values of THR was observed when APP is fixed at a high-level (3.0%). According to these results, best results were achieved for the sample F3, which has the lowest Na-Mt/FR ratio (0.67) and exhibits the greatest reduction in pHRR and THR (51 and 62% respectively), where THR is total heat release (kJ/g); “A” and “B” correspond to the Na-Mt and APP concentration (%), respectively.

$$THR = 12.86 - 0.67 \cdot A - 2.42 \cdot B + 0.40 \cdot A \cdot B \quad (2)$$

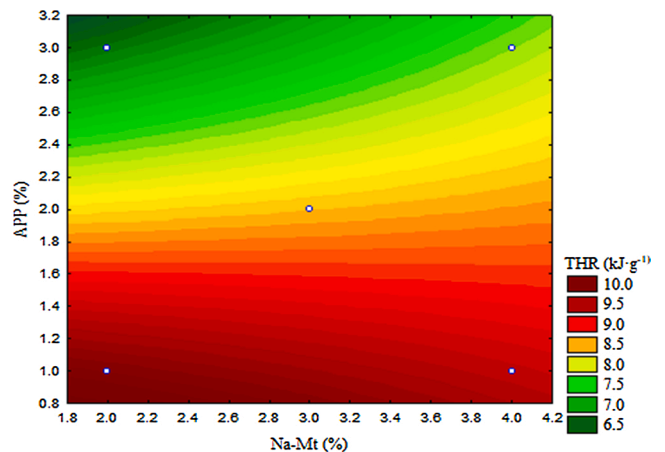


Fig. 5. Contour plot of THR (kJ/g) of the treated cotton fabric with different concentrations of APP (%) and Na-Mt (%). The contour plot clearly illustrates the influence of the APP and Na-Mt ratios in the heat release during the thermal degradation of the treated samples in the PCFC, being the region in shades of green, the best application conditions.

3.5. Tensile strength analysis

Fig. 6a shows the samples of untreated fabric (I) and the fabric containing the coating-paste (II). In both cases, the yarns in the fabric can be seen in detail due to the thin thickness of the applied film. Regarding the feel of the material, the unilateral finishing allows one side of the fabric to remain preserved, and there was no great discrepancy in the feel of the side containing the paste. The malleability of the fabric was preserved and the feel not presented any sensorial worsening. The application of the film to the fabric changed its tensile strength considerably. The tests showed an increase of about 153% in the resistance of the treated fabric compared to the untreated fabric, as shown in Fig. 6-b. All tested formulations showed similar resistance results, 48 ± 2.38 kgf, indicating that the greatest influence of the increase of resistance is attributed to the polymeric film, since the proportions of clay mineral and APP had little effect on this result. Samples F1, F2, and F4 showed the largest deviations, unlike the sample F3. The F1 sample showed the highest resistance value, the samples F2 and F4 showed the lowest values, interestingly these samples have the smallest and the largest clay mineral content, showing a tendency to decrease of the resistance with the increase of Na-Mt content.

3.5.1. Action and interaction mechanisms between the components of the coating-paste in the thermoprotective effect of treated cotton fabric

In the present study, the unilateral coating of a cotton fabric with a polymeric mixture based on poly (vinyl alcohol) (PVA) stabilized vinyl acetate-ethylene (EVA) copolymer containing APP and Na-Mt was performed, and its thermal degradation was evaluated by TGA and PCFC. Based on the results and studies reported in the literature about the mechanisms of polymers degradation, in the presence of different minerals and phosphorus-based compounds, an explanation of the possible

phenomena that occurred during the thermal degradation processes was proposed of the samples treated in this work, as illustrated in Fig. 7. Fig. 7-a illustrates the two phases of the treated sample: the face of the fabric containing the applied coating-paste and the face without application. Therefore, two possibilities of mechanism can be proposed. The first is to consider that the polymer (V323) will soften, melt and diffuse to the other side of the fabric, promoting the protection of uncoated fibers and causing both faces to have the same form of degradation due to the presence of APP. The second possibility is to consider a different degradation mechanism for each side of the fabric.

Initially, with the progressive increase in temperature, the polymeric film applied only to one side of the fabric softens and melts when reaching the state transition temperatures. The applied resin not only serves as an adherent support for the additives (Na-Mt and APP) but also acts as a vehicle for transporting them during heating. With the increase in temperature, the melted resin expands due to the release of water and volatile compounds from its matrix, the melting promotes its permeation between the fibers and yarns of the fabric [64–67]. Under heating the molten polymer begins to degrade and release some volatile compounds, the initial dehydration of the matrix begins to release water vapors, and this movement generates (at the micrometric level) the formation of bubbles that migrate to the resin surface [66,68–70], as shown in Fig. 7b. At the micrometric level, a migration phenomenon of clay mineral, and an accumulation on the resin surface begins to occur. The migration of silicates to the surface of the polymeric matrix may also occur due to the relatively low potential surface energy of the clay minerals during heating [66,68–70].

In this case, the clay mineral displacement of inside out samples is carried by temperature and viscosity gradients that create a convective movement of clay mineral orthogonal to the direction of the coating application. The movement of silicates can still be aided by numerous

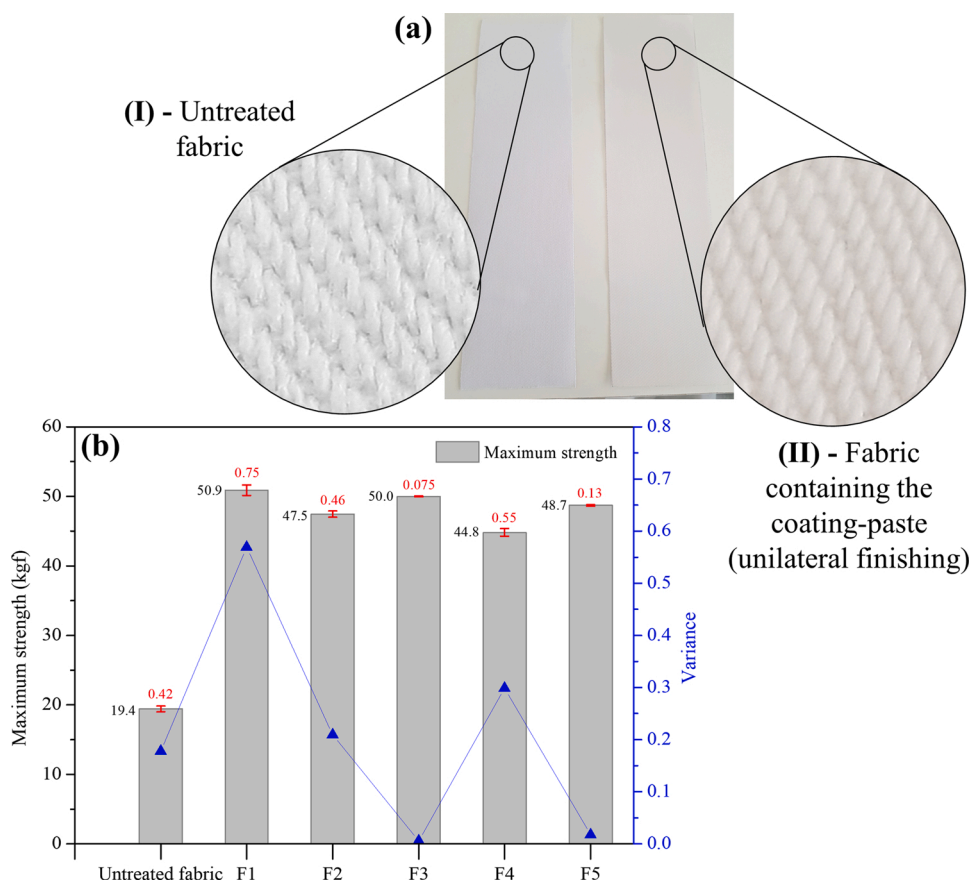


Fig. 6. (a) Aspect of the samples of untreated fabric (I) and treated fabric (containing the coating paste) (II). (b) Results of the tensile strength of the untreated fabric and treated fabric for the different formulations.

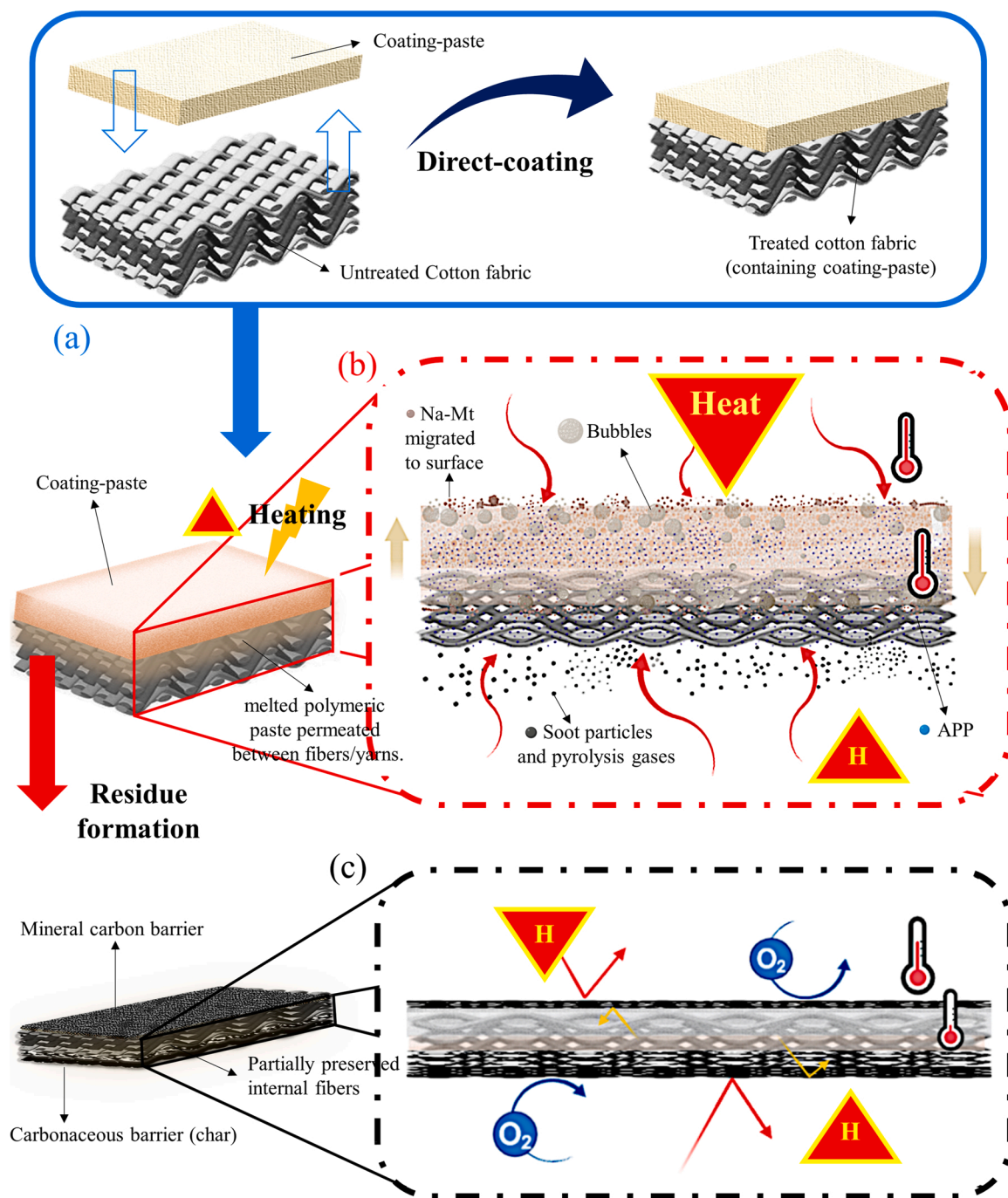


Fig. 7. Schematic illustration of the finishing characteristics applied to the cotton fabric and its behavior during the heating. (a) Unilateral deposition scheme of the coating-paste on the surface of the cotton fabric; (b) effect of heating in the coating of the sample; (c) schematic illustration of the final carbonaceous residue.

ascending bubbles that are formed in the decomposing polymer [66, 68–70]. This phenomenon contributes to the formation a protective surface barrier (Fig. 7c) generated from the polymeric decomposition, adding a mineral barrier due to the presence of the clay mineral, which decreases the heat and mass transfer between the gaseous and condensed phases [67]. At the same time, APP starts to degrade with the release of ammonia and water at lower temperatures.

It should be mentioned that the additives (Na-Mt and APP) could also interact with the coating paste which is mainly composed by PVA and EVA. Some studies in literature reported the influence of nano clays in these polymers. As mentioned in the experiments section, the preparation of the coating-paste used the previous delamination of Na-M. In this case clay mineral platelets were dispersed in the PVA/EVA matrix

(V323). Therefore, a larger surface area of interaction between the clay mineral and the molecular chains of the PVA is formed in the mixture. According to Peng and Kong [66], and Costache, Jiang and Wilkie [67] PVA and EVA have a very similar thermal degradation (Fig. 8-a), both technically degrade in two stages. When these polymers have silicates in their matrix, the first step consists of elimination reactions and chain-scission reactions (phenomenon between 330 and 375 °C in Fig. 2-b), the second step consists of allylic scission reactions (radical formation) and cyclization (phenomenon between 375 and 480 °C in Fig. 2b) [64–67].

In the PVA degradation, the first stage consists of reactions of water elimination (dehydration) and acetate groups. The first stage of EVA degradation occurs by eliminating acetate groups, as shown in Fig. 8b.

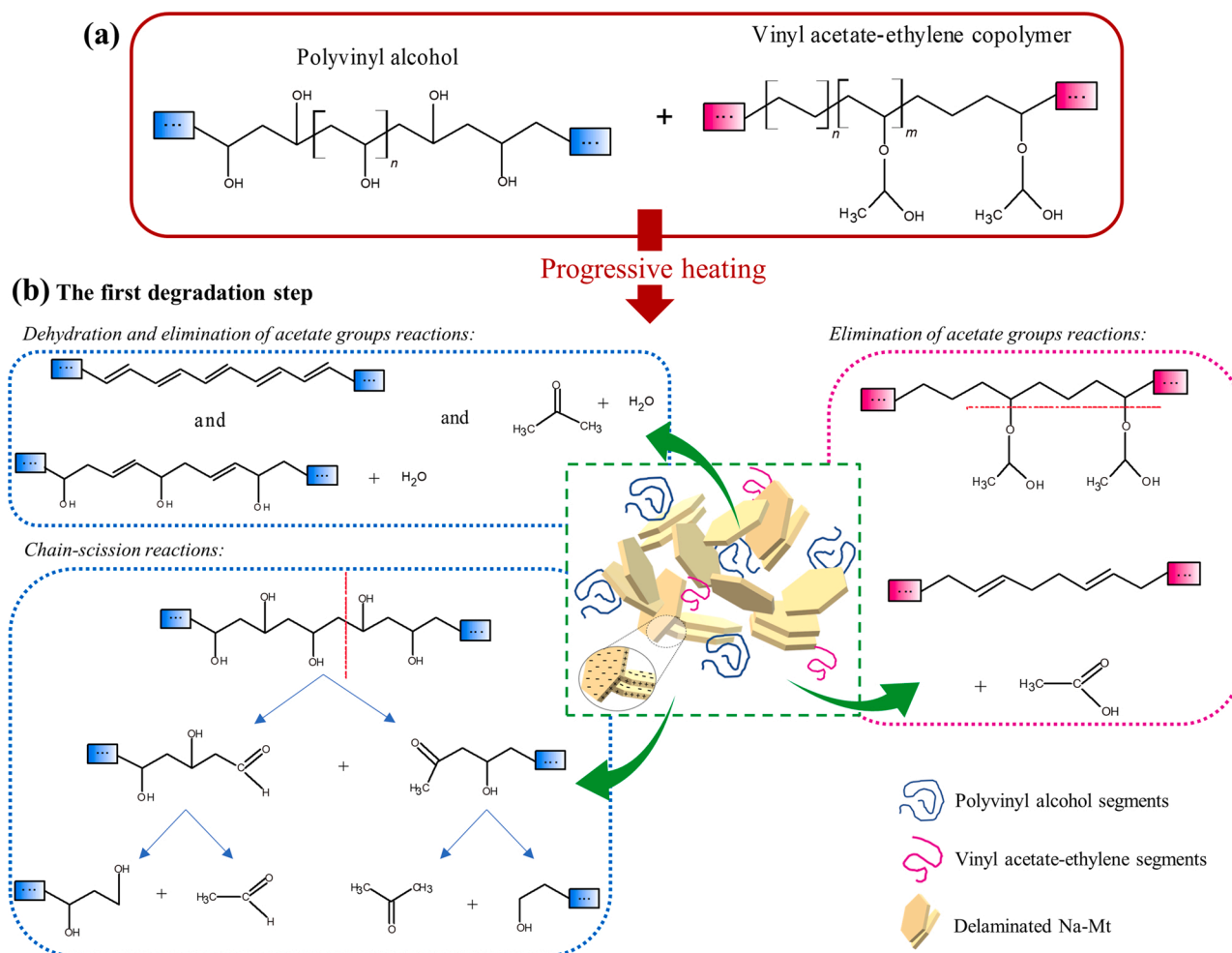


Fig. 8. Schematic illustration of the PVA and EVA thermal degradation processes of the coating paste catalyzed by the presence of delaminated montmorillonite. (a) Molecular structures of the polymers contained in the V323 mixture; (b) first stage of PVA and EVA degradation.

After this phase, PVA and EVA give rise to partially unsaturated polyene structures and release of acetic acid, the latter responsible for the greater release of gas degradation products [67]. The release of acetic acid can be accelerated by the presence of clay minerals, the catalytic effect is related to the acidic sites of the particle (hydroxyls in the edges of the lamellae) [66,67,71]. The released acetic acid can catalyze the first degradation stage of polymers, as well as non-dehydrated polyene chains that can decompose more easily at lower temperatures by chain scission, giving rise to low molecular weight by-products such as alcohols, ketones and acetaldehydes [66,67].

The second stage of degradation of these polymers is characterized by the allylic scission reactions (homolytic breaks) of the main chain (polyenes), which gives rise to the diradicals and allyl radicals, and these radicals can reorganize themselves into more stable resonance structures (secondary allylic radicals) [67,72]. The allylic radicals formed can undergo secondary reactions with the active sites of the clay minerals. The presence of nano-dispersed clay mineral platelets (delaminated Na-Mt) can limit the radicals, favoring the recombination reactions [67, 73,74]. In the absence of clay minerals, the newly formed radicals can return to the degradation cycle and go through additional scission processes. However, in the presence of clay minerals the radicals can recombine forming several branched triennials, generating reticulated structures and/or internal olefins, as shown in Fig. 9. Clay minerals can also retain linear chains and cause temporary cross-linking points [67]. The recombined radicals can also undergo cycloaddition reactions, which give rise to cyclic and aromatic structures (Diels-Alder cycloaddition) and other unsaturated structures [66,67,75]. As shown in Fig. 8,

all structures formed by transient cross-linking, radical recombination and cycloaddition participate in the formation of the carbonaceous-inorganic layer and can explain the improvement in the resistance to fiber degradation (increased residue) observed in the TGA (Fig. 2), and partially explain the variation in the maximum heat release rate observed in the PCFC (Fig. 3).

The side of the fabric that does not have the coating-paste also undergoes degradation, in this case, by a different process. For the cellulose pyrolysis, there are two reactive reactions [35–37], the first corresponds to cellulose degradation leading to char formation, and the second is related to the reactions of scission of the polymeric chain that leads to the formation of levoglucosan, as illustrated in Fig. 10 [35,37, 38]. Levoglucosan is a precursor to species of very low molecular weight and high flammability, originated from its decomposition. In the second case, volatile fuel species must react with oxygen from the surrounding atmosphere and start the flame propagation process [37]. In this case, the APP contained in the coating-paste is released with heating and decomposes releasing acidic molecules, such as phosphoric acid, that catalyzes cellulose dehydration, promoting the formation of char instead of levoglucosan [35]. A part of the phosphoric acid formed reacts with the fibers and binds to them, promoting their phosphorylation [35]. The interaction between phosphoric acid and cellulose occurs between the reactive groups of the acid and the hydroxyls of the cellulose at the C2, C3 positions and preferably at the C6 positions of the molecule [39, 76–78]. The phosphoric acid reacted directly with the hydroxyls of the cellulose, can also form bridges between the fiber molecules, causing a kind of cross-linking [39,76–78].

The second degradation step

Allylic scission reaction of polyene chain:

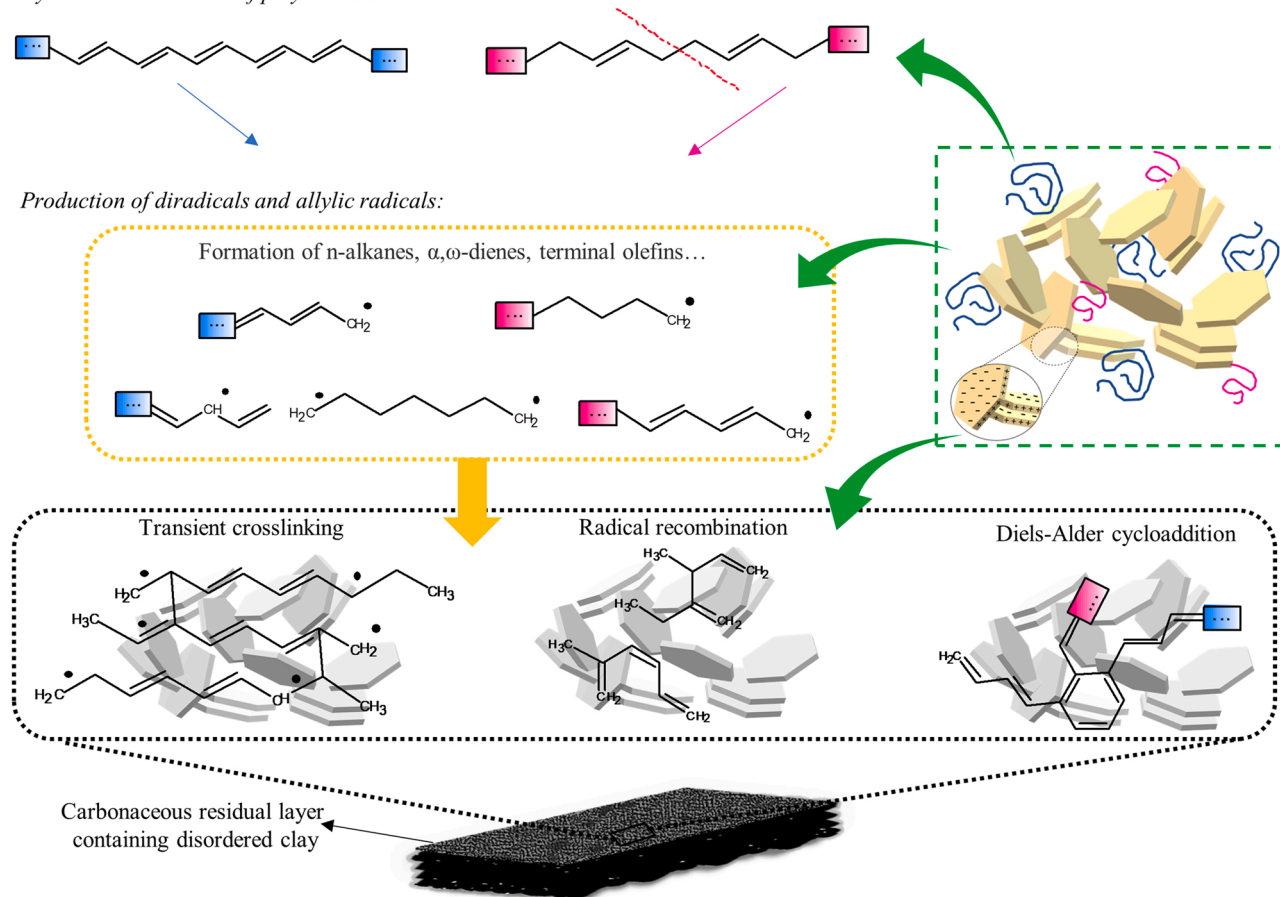


Fig. 9. Schematic illustration of the second stage of PVA and EVA thermal degradation processes catalyzed by the delaminated montmorillonite, and formation of the carbon-inorganic residue.

Higher decomposition temperatures provide greater thermal stability [79], which was not observed in the degradation of the treated fabric. The TGA analysis (Fig. 2b) shows that the cotton fibers containing the coating-paste decompose at a lower temperature compared to the untreated sample. In the literature, PVA and EVA containing silicates show an increase in thermal stability, with an increase in onset degradation temperature which was not observed in the present study. The explanation for this phenomenon is the presence of APP in the polymeric mixture applied to the fabric. The APP moves the degradation temperature of the samples to lower temperatures due to the release of phosphoric acid and its incorporation ratio has a greater influence on the thermal protection of the fibers, as shown by the results of the experimental design (Fig. 5).

4. Conclusions

In this work, a polymeric formulation containing different ratios of montmorillonite (Na-Mt) and ammonium polyphosphate (APP) was evaluated to improve the resistance to thermal degradation of a cotton fabric. The mixtures (coating-paste) were prepared in steps, under agitation with high RPM to ensure the dispersion of the clay mineral and the obtaining of a homogeneous slurry. The coating-paste was applied unilaterally on a cotton fabric using the direct-coating technique, considered a simple, cheap, and less polluting textile finishing process. The polymer used in the coating-paste had the function of keeping the dispersion stable and served as a support for the adhesion of the additives (Na-Mt and APP) on the fabric after the curing step. The addition of

the Na-Mt/APP in cotton fabric leads to a change in the thermal stability of the material. The reactions of the APP with the fiber are catalyzed by the presence of the clay mineral due to the effects of synergy and interaction between them. Under high temperature, the phosphorous compounds may interact with clay minerals, catalyze the dehydration of cellulose, followed by the formation of a carbonaceous barrier, which is able to limit the transfer of heat/combustion gases between the surrounding atmosphere and the fibers. The samples with a Na-Mt/APP ratio between 1 and 2 showed the best results concerning the residual char yield. Even the sample with the highest phosphorous content, results showed an intermediate behavior in terms of char yield and THR, indicating that some interaction between Na-Mt and APP may occur. Clay mineral performs a catalytic role in the degradation of the polymers in the paste and contributes to the formation of the surface barrier that reduces/inhibits heat and mass transfers between the gaseous and condensed phases during the pyrolysis of the fibers. The presence of Na-Mt catalyzes the degradation of APP that decomposes into phosphoric acid, which in turn accelerates the degradation of polymers and causes cellulose phosphorylation and promotes the formation of char instead of the levoglucosan. Statistical analysis showed that although the Na-Mt has no significant effect on the cotton protection to burning when applied alone, it should be considered in mixtures. The formulation and direct-coating method proposed showed potential applicability as a technique for incorporating flame retardant compounds in the finishing of cotton fabrics.

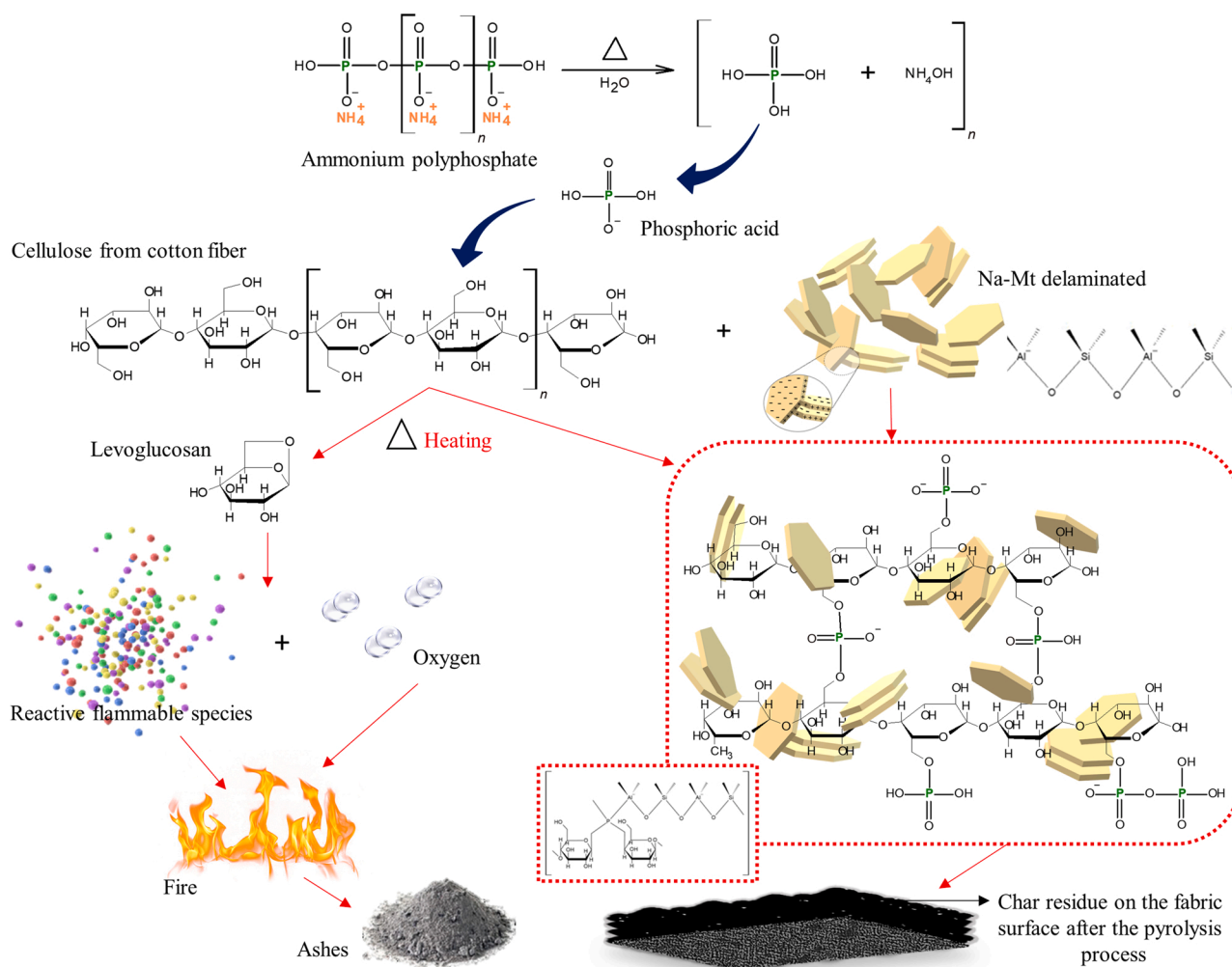


Fig. 10. Schematic illustration of the cellulose thermal degradation processes catalyzed by the delaminated montmorillonite, and formation of the carbonaceous residue.

CRediT authorship contribution statement

Carlos Rafael Silva de Oliveira: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. **Marcos Antonio Batistella:** Conceptualization, Formal analysis, Writing - review & editing, Supervision, Project administration. **Luís Antonio Lourenço:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. **Selene Maria de Arruda Guelli Ulson de Souza:** Resources, Writing - review & editing, Supervision, Funding acquisition. **Antônio Augusto Ulson de Souza:** Resources, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors report no declarations of interest.

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