



Conference Paper

Thermal Analysis of Healthy and Ecological Friendly Flame Retardants for Textiles

Albert M Manich, Sonia Perez-Rentero, Cristina Alonso, Luisa Coderch, and Meritxell Martí

Consejo Superior de Investigaciones Científicas - Instituto de Química Avanzada de Cataluña (IQAC-CSIC)

Abstract

Flame Retardants (FR) are a group of anthropogenic environmental contaminants used at a relatively high concentration in many applications. Currently, the largest marked group of FRs is halogenated FR, and many of them are considered toxic, persistent and bio accumulative. Non-halogenated alternatives are a possible solution for the problem, but there is a lack of knowledge concerning environmental impact, health risks during the production process and final use. The main objective of the LIFE-FLAREX project that supports this work, is the mitigation of the environmental and human health impact of flame retardants used in textiles, looking for new efficient more ecological and healthy alternatives, able to replace the most common FR's that include toxic compounds like halogens, formaldehyde and antimony. The aim of this work is to determine the effect of conventional and ecological flame retardants on cotton and polyester fabrics by the application of differential scanning calorimetry DSC and thermogravimetric analysis TGA. Results have been compared with those given by the best FR applied to cotton/polyester blended fabric. The application of DSC up to 550°C and TGA up to 600°C in N₂ and O₂ atmospheres give results that are in accordance with those yielded by the micro-scale combustion calorimeter. Onset temperatures of decomposition, steps of loss of mass by temperature and final residues, enable to evaluate the thermal efficiency of the different flame retardants. Results have been compared with those given by the application of ammonium polyphosphate and guanidine phosphate on cotton/polyester 50/50 blend.

Corresponding Author:

Albert M Manich

albert.manich@iqac.csic.es

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1. Introduction

The low thermal stability, easy ignition and rapid combustion of cellulose fibres represent a weaknesses and limitation in the production of fire-protective textiles when they are blended with synthetic fibres. Consequently, the application of flame retardants has been traditionally focused on their effect on cellulosic fibres. Flame retardants are applied to decrease the combustible power of textiles and favour the release of inert volatiles [1–5]. The toxicity and the environmental impact of halogenated flame retardants turn aside the interest for halogen-free flame retardants based on healthier

and environmental friendly alternatives like intumescent flame retardants (IFR) based on ammonium polyphosphate and expandable graphite that act as a blowing agent that limits mass and heat transfer, oxygen diffusion and smoke suppressor [6, 7].

The application of flame retardants in the most commonly used textiles based on polyester, cotton and their blend needs to take into account the different behaviour of the fibres to point out the effect of the flame retardants on them [8].

The application of thermal analysis techniques like differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) enables to assess the effect of the flame retardants on thermal stability and final residue at 600°C in N₂ and O₂ atmospheres. The results are in accordance with those of the heat release rate given by a micro-scale combustion calorimeter MCC related by Qin Chen and Tao Zhao [9].

The DSC diagrams of a polyester fabric will show the first sharp peak of melting about 255°C followed by a second one associated to the decomposition of polyester at temperatures above 400°C, while that of cotton will show a first peak related with the loss of humidity about 100°C followed by a second broader transition attributed to the decomposition of cotton. A slight endotherm around 220°C reveals the formation of the dehydrocellulose that is followed by an exotherm attributed to the formation of char and gaseous products. When the decomposition leads to a formation of tar, a strong endotherm appears in the range of 280 to 340°C [10]. For polyester/cotton blends the superimposition of those peaks appear. As regards the TGA plot, the decomposition of cellulose is shown by the loss of mass starting before 300°C and ending approximately at 350°C, and that of the polyester by a loss of mass that is mainly observed between 350 and 450°C approximately [11].

The objective of this work is to measure the effect of a non-halogenated FR based on dialkyl phosphono carboxylic acid amide on the thermal behaviour of cotton, the effect of decabrome diphenyl ethane including Sb₂O₃ and that of expandable graphite on the thermal behaviour of polyester and compare the results with those given by the ammonium polyphosphate and guanidine phosphate, on the thermal behaviour of a polyester/cotton fabric [12, 13].

2. Materials and Methods

The reference materials used for the application of the different flame retardants were the following:

- 1) Cotton linen white fabric: Plain weave of approximately 100 g/m² of mass per unit area.

2) Polyester upholstery fabric made by white and black warp yarns and red weft yarns of different linear densities resulting in a fabric of approximately 350 g/m^2 of mass per unit area.

3) Polyester/cotton 50/50 mattress ticking fabric: Plain weave of approximately 180 g/m^2 mass per unit area.

The application of the different flame retardants on reference materials resulted in the following samples:

- a) Cotton linen (reference material)
- b) Cotton linen treated with dialkyl phosphono carboxylic acid amide (add-on 0.7%)
- c) Polyester upholstery (reference material)
- d) Polyester upholstery treated with decabrome diphenyl ethane + Sb_2O_3 (add-on 11.5%)
- e) Polyester upholstery treated with expandable graphite (add-on 35%)
- f) Polyester/cotton mattress ticking (reference material) [12]
- g) Polyester/cotton mattress ticking treated with guanidine phosphate (add-on 20%) [12]
- h) Polyester/cotton mattress ticking treated with ammonium polyphosphate (add-on 15%) [12]

The DSC analysis was conducted in a Mettler-Toledo DSC-823 apparatus using samples of about 3 mg placed in micro perforated aluminium pans for internal pressure control, in order to let the water and other volatiles be completely removed from testing pans [12]. Tests were conducted from 30°C to 500°C at $10^\circ\text{C}/\text{min}$ under 50 mL/min of N_2 flux.

The TGA analysis was performed in a Mettler-Toledo TGA/SDTA 840 using samples of about 10 mg placed in completely open aluminium pans. Tests were conducted from 25°C to 600°C at $10^\circ\text{C}/\text{min}$ under a N_2 flux of 60 mL/min and O_2 flux of 60 mL/min [12].

3. Results and Discussion

3.1. Cotton linen fabric

Figure 1 shows the DSC plot and the TGA plots conducted in N_2 and O_2 atmospheres of the cotton linen fabric. The DSC shows the first peak mainly due to the evaporation of water in cotton at 122.9°C followed by that of the decomposition that begins at about

250°C reaching a maximum near 350°C that can be attributed to the formation of char and gaseous products.

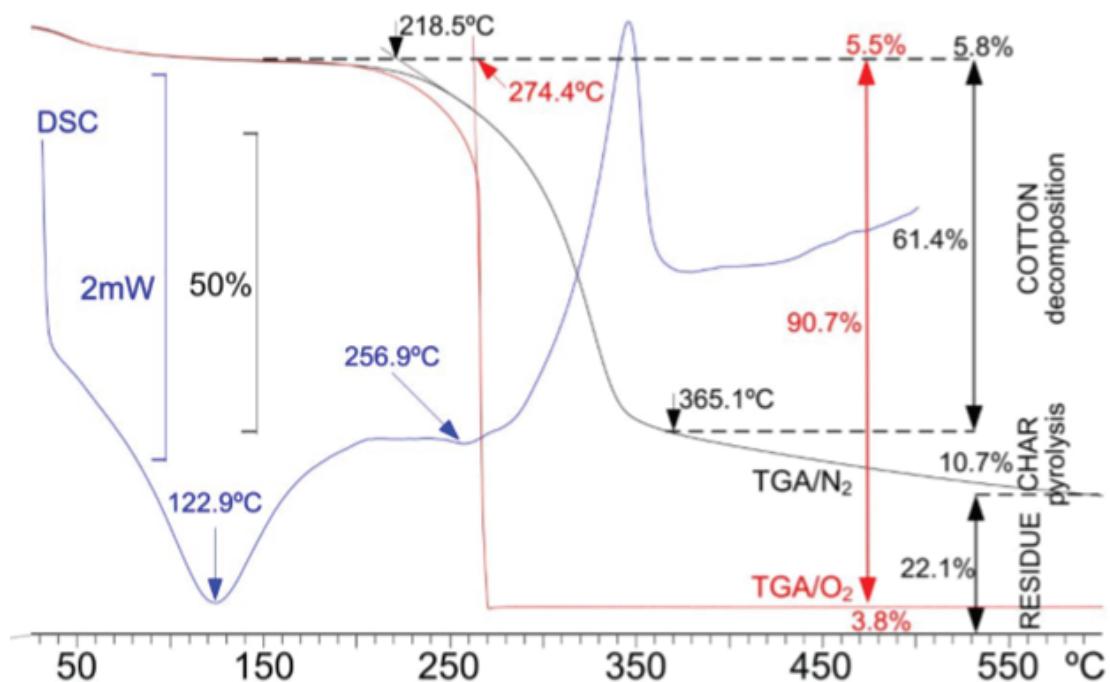


Figure 1: DSC and TGA plots of the cotton linen white fabric

The TGA shows the onset temperature of decomposition between 218 and 275°C depending on the atmosphere (N_2 or O_2). The DTGA identifies the first fast mass loss step attributed to the decomposition of cellulose until 365.1°C (in N_2) or 274.4°C (in O_2) with a mass loss of 61.4% (in N_2) or 90.7% (in O_2). The decomposition of cellulose in N_2 is followed by second loss of mass that could be attributed to char pyrolysis up to 600°C with a 10.7% of mass loss, leading to a final residue at 600°C of 22.1%. The final residue in O_2 is 3.8%.

The application of a flame retardant based on dialkyl phosphono carboxylic acid amide just affects the thermal transitions of the cotton linen fabric by increasing the onset temperature of decomposition in 20°C (in O_2) or 80°C (in N_2). Figure 2 shows the DSC plot and the TGA plots conducted in N_2 and O_2 atmospheres of the cotton linen fabric. No great differences are observed in the loss of mass corresponding to cotton decomposition, char pyrolysis in N_2 atmosphere and final residue at 600°C. The application of flame retardant slightly decreases the absorption of water of the cotton fabric.

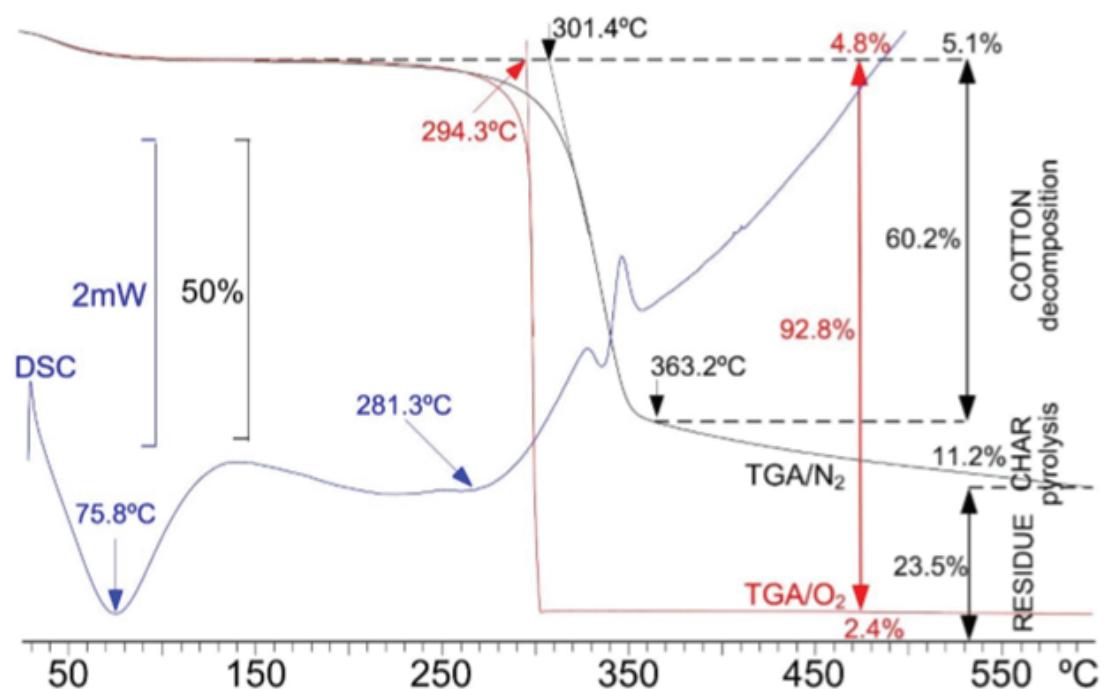


Figure 2: DSC and TGA plots of the cotton linen fabric treated with dialkyl phosphono carboxylic acid amide as flame retardant.

3.2. Polyester upholstery fabric

As regards the polyester fabric for upholstery, Figure 3 shows the DSC plot and the TGA plots conducted in N₂ and O₂ atmospheres. The DSC plot enables to identify the peak of PES melting at 255.6°C followed by an endo-exo transition that can be attributed to the PES decomposition.

The TGA shows the onset temperature of decomposition after melting at 334.3°C and 348.8°C depending on the atmosphere (N₂ or O₂). The DTGA identifies two steps in the decomposition of polyester in N₂. The first one up to 375.5°C followed by a second one up to 478°C accounting for a 82.7% of the loss of mass. In O₂ atmosphere a first step of decomposition is observed until 462.7°C followed by a second one probably due to oxidation reactions up to 520°C accounting for a loss of 98.4% of mass loss. The final residue at 600°C is 13.5% in N₂ and 0.6% in O₂.

The application of a flame retardant based on decabromo diphenyl ethane including Sb₂O₃ increases the onset temperature of decomposition by 10°C in O₂ and by 75°C in N₂. No relevant differences are observed in the loss of mass and the final residues in O₂ and N₂ atmospheres as shown in Figure 4.

When expandable graphite is used as ecological intumescent flame retardant, the effect on thermal behaviour is different from that observed for conventional flame retardants as shown in Figure 5. Its application leads to a decrease in the onset

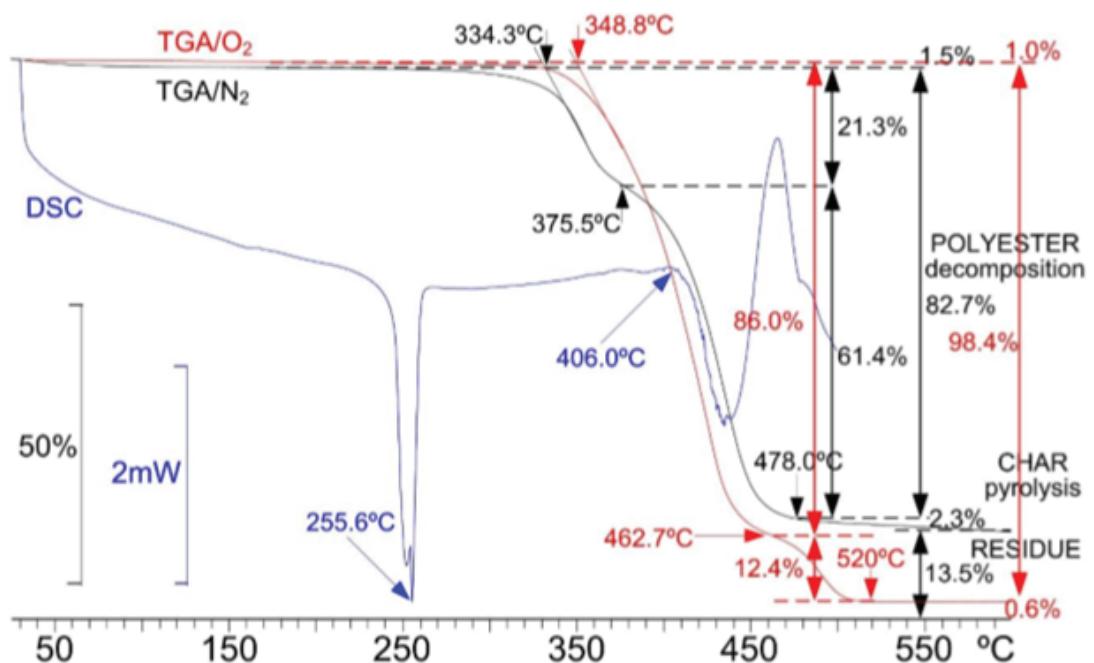


Figure 3: DSC and TGA plots of the polyester fabric for upholstery

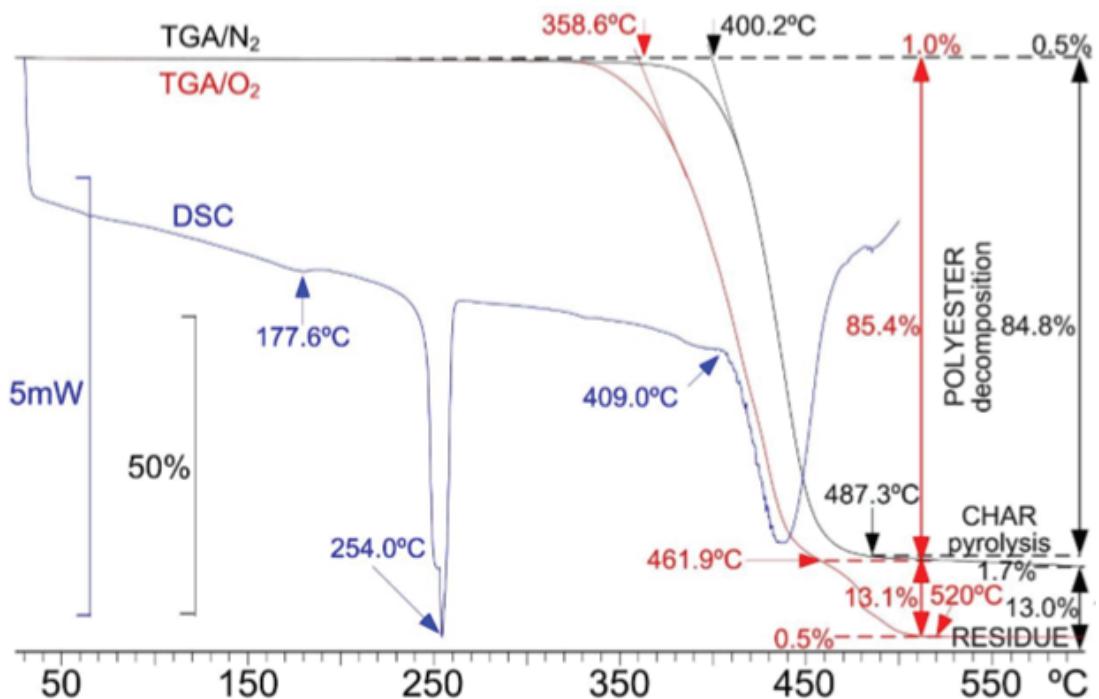


Figure 4: DSC and TGA plots of the polyester upholstery fabric treated with decabromo diphenyl ethane including Sb₂O₃ as flame retardant.

temperature of decomposition, although a short first step of mass loss is observed. The main protective effect of the expandable graphite appears from 313°C at the DSC with a wide endotherm attributed to the graphite expansion that protects polyester and greatly reduces the loss of mass due to decomposition resulting in a significant increase

on final residue (35.7% in O₂ and 44.5% in N₂). It cannot be discarded that one of the main components of the residue is the expandable graphite.

3.3. Polyester/Cotton 50/50 Mattress ticking fabric

Figure 6 shows the DSC plot and the TGA plots conducted in N₂ and O₂ atmospheres of the polyester/cotton 50/50 mattress ticking. The DSC plot enables us to identify a first peak mainly due to the evaporation of water in cotton at 117.2°C followed by that of PES melting at 253.3°C. The main step of cotton degradation is identified by the endo-exo effect located between 333.3°C and 350.4°C. Finally, the endotherm which can be attributed to PES degradation is observed at 446.0°C.

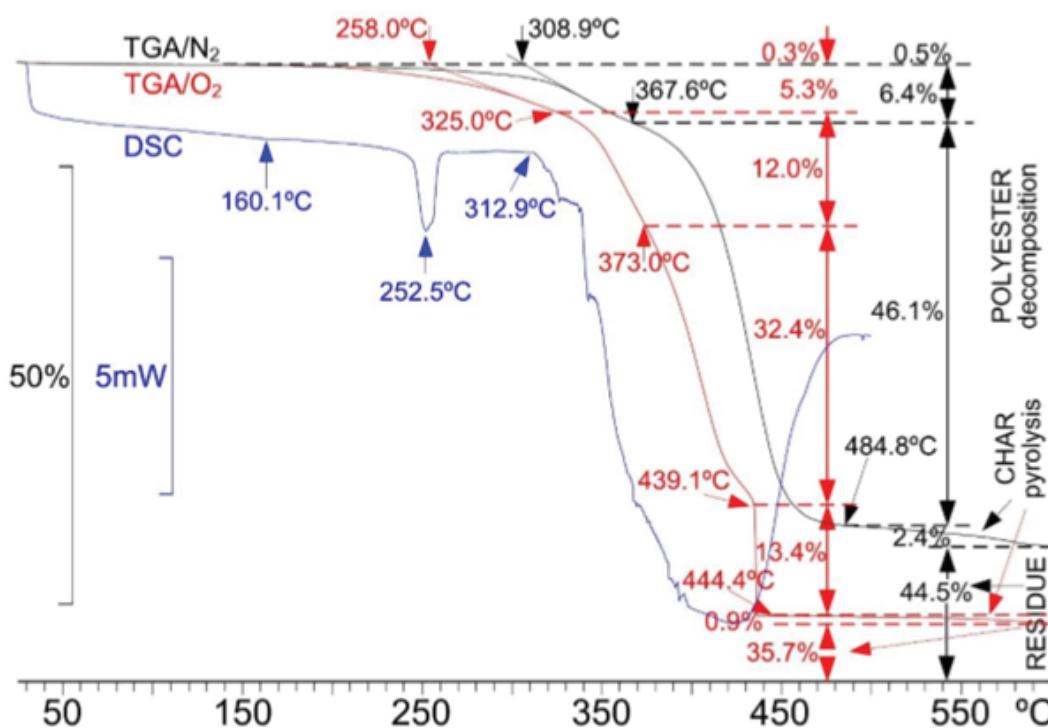


Figure 5: DSC and TGA plots of the polyester upholstery fabric treated with expandable graphite as ecological intumescent flame retardant

The TGA shows the onset temperature of cotton decomposition (after PES melting) at 263.5°C in O₂ or at 311.1°C in N₂. The DTGA identifies the first fast mass loss step attributed to cellulose decomposition until 356.8°C in O₂ or 375.3°C in N₂ with a mass loss of 44.6% in O₂ or 39.3% in N₂.

Two ecological flame retardants have been applied to the polyester/cotton mattress ticking. The first one is based on guanidine phosphate. Figure 7 shows the DSC and TGA results of this application.

The DSC shows two first peaks before that expected of the polyester melting, at 127.0°C and 209.2°C that can be associated to moisture and the beginning of cellulose degradation that accounts for a loss of mass shorter than 3%. Then clearly appears the peak of polyester melting at 252.5°C. It is known that guanidine phosphate melts in a region between polyester melting and the marked exotherm at 283.4°C, that could be caused by the formation of a new more stable reorganization of the polyester promoted by the guanidine phosphate including a possible participation of cellulosic components. As temperature increases two other marked endotherms follow at 348.0°C and 394.3°C being the former mainly attributed to cellulose decomposition and the latter to polyester decomposition.

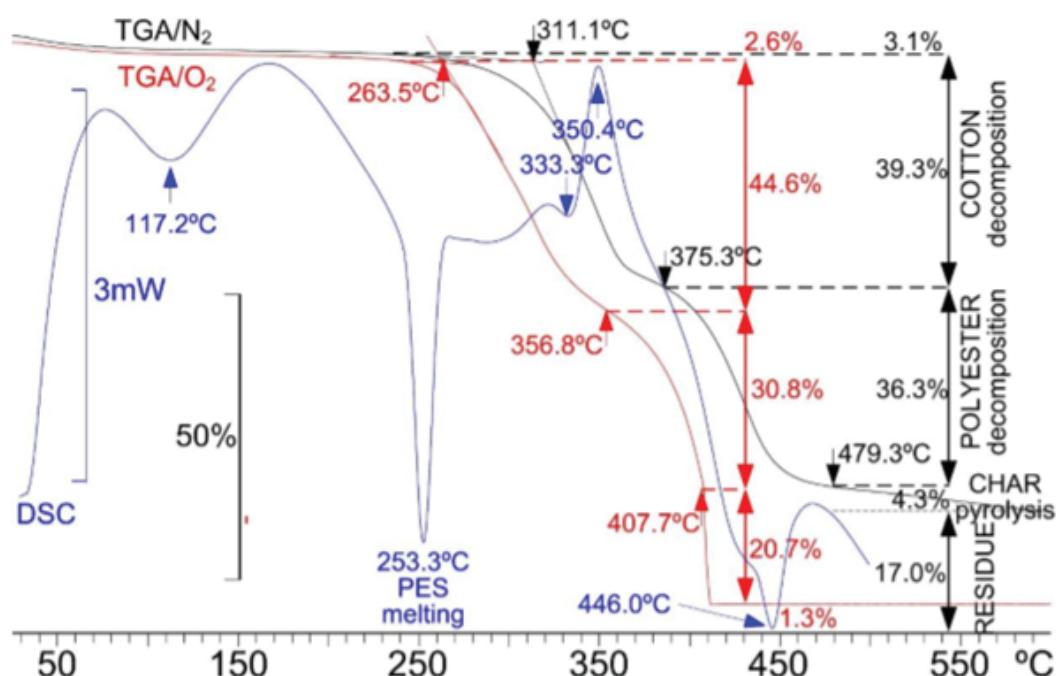


Figure 6: DSC and TGA plots of the polyester/cotton 50/50 mattress ticking

As regards the TGA curves, it can be seen that the melting of polyester and the exotherm due to the formation of a new structure by the presence of the guanidine phosphate is overlapped with the decomposition of cellulose that accounts for a mass loss of about 27-29% in two steps, followed by the loss of mass corresponding to the polyester decomposition, that accounts for an additional 36-41% reaching the final step of char pyrolysis that accounts for a final loss of mass of 2.9% in N₂ and 15.5% in O₂ leading to a final residue of 27.5% in N₂ and 12.3% in O₂.

When the other ecological and intumescent flame retardant based on ammonium polyphosphate is applied the results of DSC and TGA plot are shown in Figure 8. The flame retardant activity of the ammonium polyphosphate commences at lower

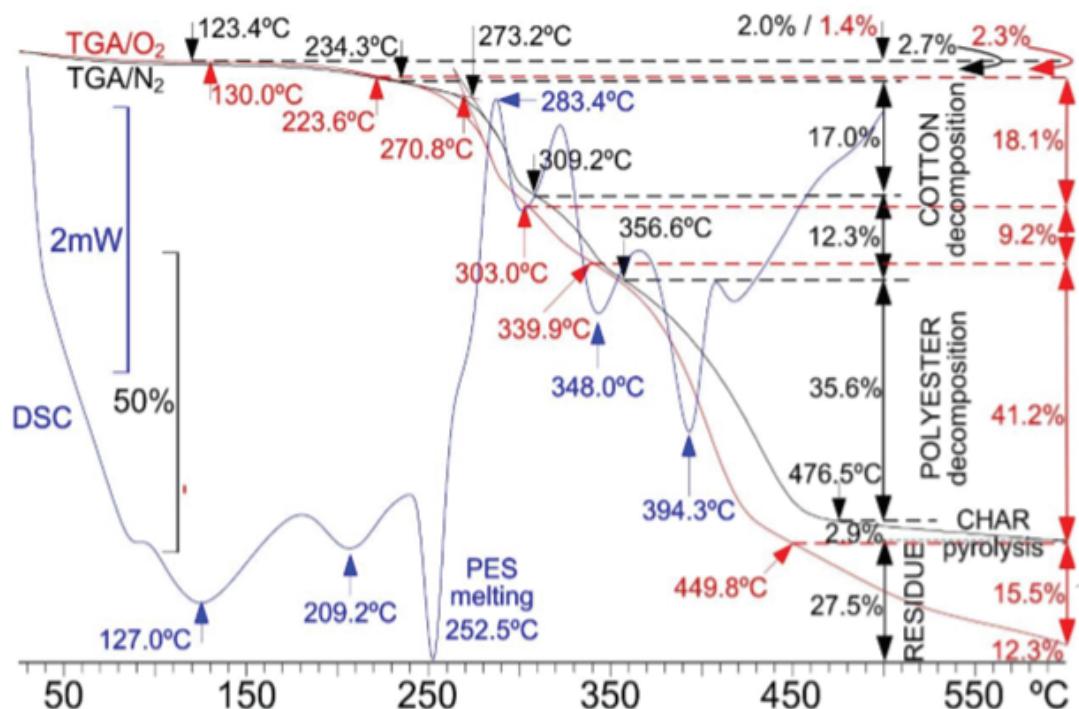


Figure 7: DSC and TGA plots of the polyester/cotton mattress ticking treated with an ecological flame retardant based on guanidine phosphate.

temperatures. The first stage of decomposition is shown by a small weight loss at about 200 °C, probably due to partial degradation of the crystalline form that changes to a more stable form accompanied by cross-linking and loss of some NH₃. This process is shown by an endotherm about 185°C [11], the peak that appears at the DSC plot at 185.2°C, that explain the new configuration of the ammonium polyphosphate and, probably, the degradation of amorphous cellulose. The sudden peak of the polyester melting is observed at 253.1°C that is overlapped with the degradation of cellulose that has begun before. The second peak at 262.1°C and the adjacent exotherm at 272.9°C enable to suppose the formation of a new more stable crystalline configuration of polyester promoted by the ammonium polyphosphate including the participation of cellulosic components. As temperature increases a marked endotherm appears at 411.8°C caused by the degradation of the new more stable polyester structure.

As regards the TGA curves, it can be seen that the melting of polyester and the exotherm due to the formation of a new structure promoted by ammonium polyphosphate is overlapped with the decomposition of cellulose that has begun around 250°C. The loss of mass due to cellulose degradation accounts for the 25% of mass loss, added to the initial loss of about 5% explained by the ammonium polyphosphate and probably amorphous cellulose. The cellulose degradation is followed by the loss of mass corresponding to the polyester decomposition (38% in N₂ and 43% in O₂ of mass

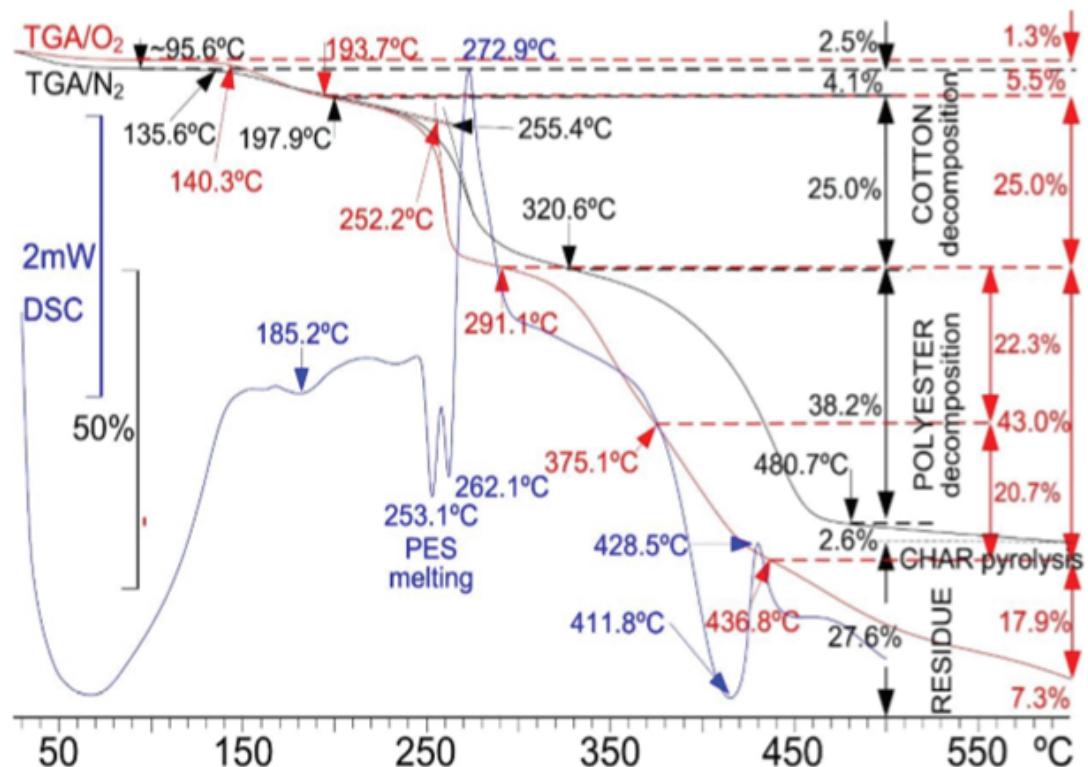


Figure 8: DSC and TGA plots of the polyester/cotton mattress ticking treated with an ecological and intumescent flame retardant based on ammonium polyphosphate

loss), reaching the final step of pyrolysis with a loss of mass of 2.6% in N₂ atmosphere and 17.9% in O₂ atmosphere, leaving a final black residue that also greatly depends on the atmosphere, 27.6% in N₂ and 7.3% in O₂ respectively. Table 1 summarises the onset temperatures and the final residue at 600°C of the fabrics according to the composition and the flame retardant applied given by the TGA.

4. Conclusions

The application of both the differential scanning calorimetry up to 500°C and the thermogravimetric analysis TGA up to 600°C in O₂ and N₂ atmospheres enable us to evaluate the effect of the flame retardants on the thermal behaviour of cotton, polyester and polyester/cotton blended fabrics.

The effect of the ecological flame retardant based on dialkyl phosphono carboxylic acid amide on cotton yields to an ascension on the onset temperature of decomposition. Final residues at 600°C regardless testing atmosphere are similar to those given by the untreated cotton fabric.

TABLE 1: Onset temperature of decomposition in °C and final residue at 600°C in % of the different fabrics and flame retardants applied given by the TGA, according to the atmosphere (O₂ or N₂).

Results given by the TGA	Onset temperature of decomposition / °C		Final residue at 600°C / %	
	in O₂	in N₂	in O₂	in N₂
Reference fabric + flame retardant applied				
Cotton linen fabric	274.4	218.5	3.8	22.1
CO + dialkyl phosphono carboxylic acid amide	294.3	301.4	2.4	23.5
Polyester upholstery fabric	348.8	334.3	0.6	13.1
PES + decabrome diphenyl ethane with Sb ₂ O ₃	358.6	400.2	0.5	13.0
PES + Expandable graphite	258.0	308.9	35.7	44.5
Polyester/cotton 50/50 mattress ticking	263.5	311.1	1.3	17.0
PES/CO + Guanidine phosphate	270.8	273.2	12.3	27.5
PES/CO + Ammonium polyphosphate	252.2	255.4	7.3	27.6

The effect of the conventional flame retardant on polyester based on decabrome diphenyl ethane including Sb₂O₃ yields to ascend on the onset temperature of decomposition. Final residues at 600°C regardless testing atmosphere are practically the same to those given by the untreated polyester fabric.

The effect of the ecological flame retardant based on guanidine phosphate on polyester/cotton are mainly based on the significant increase of the final residue yielding the lowest loss of mass in polyester decomposition and char pyrolysis regardless the atmosphere, while the effect on the onset temperature of decomposition are shorter than those of the conventional and ecological flame retardants applied to cotton and polyester fabrics.

The effect of the ecological intumescence flame retardant on polyester fabric and based on expandable graphite slightly decreases the initial temperatures of decomposition regardless the atmosphere and yields the highest increase in the final residue at 600°C (35.7% in O₂ and 44.5% in N₂).

The effect of the ecological intumescence flame retardant on cotton/polyester fabric and based on ammonium polyphosphate showed the highest protective effect on cotton. It decreases the initial temperature of decomposition favouring the release of inert volatiles and increases the final residue at 600°C (7.3% in O₂ and 27.6% in N₂).

The ammonium polyphosphate showed the highest protective effects on cotton, because it causes the highest reduction in the initial temperature of decomposition and on the corresponding loss of mass regardless the atmosphere. Its protective effect on

the polyester component is lower than that caused by guanidine phosphate explained by the lower final residue in O₂ atmosphere, and greater loss of mass in polyester degradation and char pyrolysis regardless the atmosphere.

Depending on the final application of textiles (clothing, upholstery, home textiles) guanidine phosphate and expandable graphite can be considered as good potential ecological alternatives to the conventional FR's.

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References

- [1] Manich A. (1961). *A prestos y acabados de fibras textiles*. (Barcelona: Dalmau y Jover), pp.267-269.
- [2] Hendrix, J.E., Drake, G.L., Barker R.H. (1972). "Pyrolysis and combustion of cellulose. III. Mechanistic basis for the synergism involving organic phosphates and nitrogenous bases". *Journal of Applied Polymer Science*, vol. 16, pp. 41-59.
- [3] Basak, S. and Samanta, K.K (2019). "Thermal behaviour and the cone calorimetric analysis of the jute fabric treated in different pH condition". *Journal of Thermal Analysis and Calorimetry*, vol. 135, pp. 3095-3105.
- [4] El-Shafei, A., ElShemy, M., and Abou-Okeil A. (2015). "Eco-friendly finishing agent for cotton fabrics to improve flame retardant and antibacterial properties". *Carbohydrate Polymers*, vol. 118, pp. 83-90.
- [5] Zhu, P., Sui, S., Wang, B., et al. (2004). "A study of pyrolysis and pyrolysis products of flame-retardant cotton fabrics by DSC, TGA, and PY-GC-MS". *Journal of Analytical and Applied Pyrolysis*, vol. 71, pp. 645–655.
- [6] Guo, C., Zhon, L., and Lv, J. (2013). "Effects of Expandable Graphite and Modified Ammonium Polyphosphate on the Flame-Retardant and Mechanical Properties of Wood Flour-Polypropylene Composites2. *Polymers & Polymer Composites*, vol 21, issue 7, pp. 449-456.
- [7] Xu, L., Wang W., and D Yu (2017) "Durable flame retardant finishing of cotton fabrics with halogen-free organophosphonate by UV photoinitiated thiol-ene click chemistry". *Carbohydrate Polymers*, vol. 172, pp.275–283.

- [8] Alongi, J., Ciobanu, M., Tata, J., et al. (2011) "Thermal stability and flame retardancy of polyester, cotton, and relative blend textile fabrics subjected to sol–gel treatments". *Journal of Applied Polymer Science*, vol. 119, pp.1961-1969.
- [9] Chen, Q. and Zhao, T. (2015). "The thermal decomposition and heat release properties of the nylon/cotton, polyester/cotton and Nomex/cotton blend fabrics". *Textile Research Journal*, vol. 86, pp.1859-1868.
- [10] Manich, A.M., and Ussman Eds., M.H. (2002). *Updating the 'cottonized' flax processing*. (Covilhã: Universidade da Beira Interior), pp 178-191.
- [11] Davies, P.J., Horrocks, A.R., and Alderson A. (2005). "The sensitisation of thermal decomposition of ammonium polyphosphate by selected metal ions and their potential for improved cotton fabric flame retardancy". *Polymer Degradation and Stability*, vol. 88, pp. 114-122.
- [12] Manich, A.M., Alonso, C., Pérez-Rentero, S., et al. (2019). Thermal Analysys (DSC, TGA) of textile flame retardants with lower environmental impact. *AUTEX2019, 19th World Textile Conference on Textiles at the Crossroads*. Ghent, Belgium.
- [13] Siriviriyam, A., O'Rear, E.A., and Yanumet, N. "The effect of phosphorus content on the thermal and the burning properties of cotton fabric coated with an ultrathin film of a phosphorus-containing polymer". *Polymer Degradation and Stability*, vol. 94, pp.558-565.