THERMAL ANALYSIS (DSC, TGA) OF TEXTILE FLAME RETARDANTS WITH LOWER ENVIRONMENTAL IMPACT

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EXTENDED ABSTRACT

Key Words: DSC, TGA, Flame retardants, textiles, cotton/polyester

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 focussed on their effect on cellulosic fibres. A great number of flame retardants have been used in order to decrease the combustible power of textiles and favour the release of inert volatiles [1]. The toxicity and the environmental impact of flame retardants based on bromide, formaldehyde and antimony, turn aside the interest for flame retardants based on other more healthy and environmental friendly alternatives.

The application of flame retardants in the most common used polyester/cotton blends needs to be into account the different behaviour of both components when blended. The application of thermal analysis techniques like differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) lead to results that, according to Qin Chen and Tao Zhao [2], are in accordance with those of the heat release rate given by a micro-scale combustion calorimeter MCC.

The DSC diagrams of a polyester/cotton will show the first sharp peak of polyester melting about 255ºC, a second broader peak attributed to the decomposition of cotton around 360ºC, and a third one associated to the decomposition of polyester at temperatures above 400ºC.

The TGA curves will draw two stages: the first starting around 310ºC and ending approximately at 380-390ºC, caused by the decomposition of cellulose, and the second from there until 470-485ºC, which is mainly attributed to the decomposition of polyester [2].

The objective of this work is to evaluate the effect of three different non toxic and more environmental friendly flame retardants based on ammonium sulfamate, ammonium polyphosphate and guanidine phosphate, on the thermal behaviour of a polyester cotton 50/50 fabric through the application of TGA and DSC thermal techniques.

2. MATERIALS AND METHODS

A plain weave mattress ticking of polyester/cotton 50/50 fabric of 177 g/m² mass per unit area was used to apply the flame retardants resulting in the following different samples:

a) NT CO PES 50/50: the untreated mattress ticking used as reference material.

b) Flarex004-047: the mattress ticking containing 11 wt% of the flame retardant Ecoflam TP3928 supplied by Sigma Aldrich, based on ammonium sulfamate.

c) Flarex004-020: the mattress ticking taking up 20 wt% of the flame retardant Addiflam PP50 supplied by CTF2000, based on guanidine phosphate.

d) Flarex005-3: the mattress ticking absorbing 15 wt% of the flame retardant Pekoflam MSP supplied by Vickers Laboratories Ltd, based on ammonium polyphosphate.

The DSC analysis was conducted in a Mettler-Toledo DSC-823 apparatus using samples of about 3 mg placed in microperforated aluminium pans for internal pressure control, in order to let the water and other volatiles be completely removed from testing pans [3]. Tests were conducted from 30ºC to 500ºC at 10ºC/min under 50 mL/min of N2 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 25ºC to 600ºC at 10ºC/min under a N_2 flux of 60 mL/min and O_2 flux of 60 mL/min.

3. RESULTS AND DISCUSSION

Figure 1 shows the DSC plot and the TGA plots conducted in N2 and O2 atmospheres. The DSC plot enables us to identify a first peak mainly due to the evaporation of water in cotton at 117.2ºC followed by that of the PES melting at 253.3ºC (enthalpy ΔHm 26.3 J/g), the main step of cotton degradation that shows an endotherm at 333.3ºC followed by an exotherm at 350.4ºC. Finally, the endotherm which can be attributed to PES degradation at 446.0ºC.
The TGA shows the onset temperature of cotton decomposition (after PES melting) at 263.5ºC or 311.1ºC depending on the atmosphere (O2 or N2). The DTGA identifies the first fast mass loss step attributed to the decomposition of cellulose until 356.8ºC (in O2) or 375.3ºC (in N2) with a mass loss of 44.6% (in O2) or 39.3% (in N2).
When these temperatures are overcome a second faster loss corresponding to the decomposition of PES appears accounting for a 30.8% in O2 up to 407.7ºC, and 36.3% in N2 up to 479.3ºC. The last step of char pyrolysis yields a mass loss of 20.7% (in O2) or 4.3% (in N2).
The thermal degradation up to 600ºC leaves a remaining white residue of 1.3% (in O2) or a black residue of 17% (in N2).

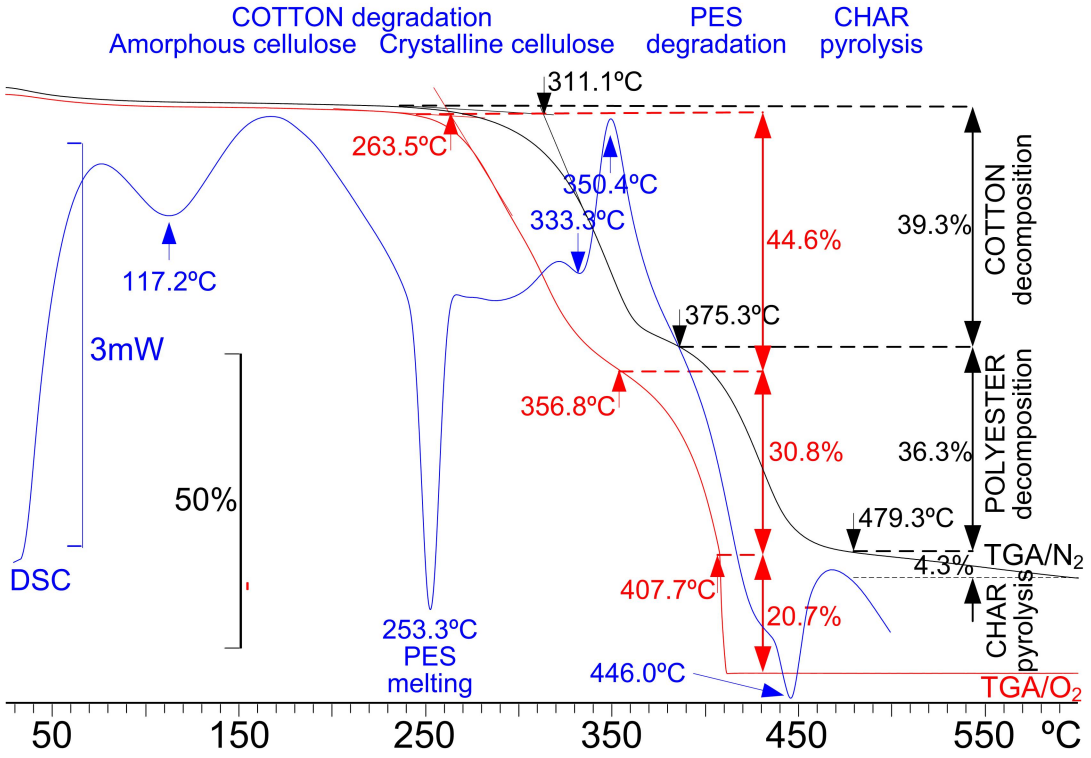

Figure 1: DSC and TGA plots in N2 and O2 atmospheres of the untreated mattress ticking of polyester/cotton plain weave of 177 g/m².

The main results given by the differential scanning calorimetry are summarized in Table 1. Peak temperatures that identify relevant exothermal (structural reordering configuration) and endothermal (melting or degradation) processes are shown, including an estimation of the melting enthalpy of polyester.

Table 1: DSC analysis of the non treated CO/PES sample and those treated with ammonium sulfamate FL004-047, guanidine phosphate FL004-020 and ammonium polyphosphate FL005-3: PES melting peak temp. Tm and enthalpy ΔHm, and peak temperatures of the exo and endotherms attributed to flame retardant-CO configuration $TpCO_{exo}$, cotton degradation $TpCO_{endo}$, PES reconfiguration $TpPES_{exo}$ and PES degradation $TpPES_{endo}$.

Samples /	PES melting		CO transitions		PES transitions	
Thermal transitions	Tm	ΔHm	$TpCO_{exo}$	$TpCO_{endo}$	$TpPES_{exo}$	$TpPES_{endo}$
Untreated CO/PES fabric	253.3ºC	26.3J/g	-	335.9ºC	-	428.5ºC
FL004-047 Amm.sulf.	251.7ºC	46.0J/g	239.7ºC	-	-	433.8ºC
FL004-020 Guan.phosph.	252.5ºC	11.0J/g	-	-	283.4ºC	394.3ºC
FL005-3 Amm.polyphosph.	253.1ºC	9.4J/g	-	262.1ºC	269.5ºC	415.0ºC

As regards the thermo gravimetrical analysis in N2 and O2 atmospheres, the most relevant results are given in Table 2.

Table 2: TGA analysis up to 600ºC of the non treated CO/PES sample and those treated with ammonium sulfamate FL004-047, guanidine phosphate FL004-020 and ammonium polyphosphate FL005-3 in N_2 and O_2 atmospheres: Initial temperature of decomposition $\mathbf{Td_i}$ and relative loss of mass $\Delta\mathbf{m_i}$ of the three steps mainly related with cotton decomposition, polyester decomposition and char pyrolysis, the final temperature of decomposition $\mathbf{Td_{end}}$ and the relative final mass of the residue at 600ºC $\mathbf{m_{f600}}$.

		Cotton decomposition / Polyester decomposition / Char pyrolysis / Residue							
Samples	Atmosph.	Td_1/ºC	Δm_1/%	Td_2/ºC	Δm_2/%	Td_3/ºC	Δm_3/%	Td_{end}/ºC	m_{f600}/%
Untreated	N_2	311.1	39.3	375.3	36.3	479.2	4.3	600	17.0
CO/PES	O_2	263.5	44.6	356.8	35.9	407.7	20.7	410	1.3
Amm.sulf.	N_2	240.6	30.5	341.6	35.7	476.6	4.6	600	25.4
FL004-047	O_2	238.9	29.6	286.7	15.6	364.1	51.9	393	1.4
Guan.phos.	N_2	234.4	29.3	356.7	35.6	476.5	2.9	600	27.5
FL004-020	O_2	223.6	27.3	339.9	41.2	449.8	15.5	600	12.3
Amm.polyph.	N_2	197.2	25.0	320.6	38.2	480.7	2.6	600	27.6
FL005-3	O_2	193.7	25.0	291.1	43.0	436.8	17.9	600	7.3

4. CONCLUSIONS

The application of guanidine phosphate and ammonium polyphosphate causes a significant decrease in the melting enthalpy of polyester followed by an exothermal peak that can be related with a more stable polymorphic form of the polymer. The initial temperatures of decomposition are lowers than that observed with ammonium sulfamate, leading to a significant increase to the final black residue in N_2 athosphere, being the highest in O_2 atmosphere that yielded by the guanidine phosphate, which appears to be the flame retardant less affected by the testing atmosphere.

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