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Thermal Stability of Polyester Fabric with Polyacrylic Coatings

DOI: 10.5604/12303666.1152734

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Abstract
The aim of the study was to assess the thermal properties of polyester (PET) woven fabrics with unmodified (PET/AC) and flame-retardant modified (PET/AC/FR) polyacrylic coatings, before and after 1, 5, 10 & 15 washes. Differential scanning calorimetry DSC and thermogravimetric TG/DTG analyses were carried out in order to investigate the thermal processes. To evaluate the effects of the modifications and washing treatment, the scanning electron microscopy SEM/EDS technique was used. The flame-retardant modification caused that the melting enthalpy and the initial thermal degradation temperature decreased and the thermal degradation heat increased. The washing of PET/AC and PET/AC/FR fabrics caused an increase in the melting enthalpy by approximately 12% and 63% and a decrease in thermal degradation heat by about 2% and 15%, respectively. It was found that the flame-retardants were rinsed out from the coating after the fifth wash.

Key words: *textiles, polymers, coating, flame-retardant, DSC, TG/DTG.*

Introduction

The aim of the functional modification of textile materials is to change their physical, chemical and biological properties [1 - 6]. One of the ways to modify textile materials is the application of polymer coatings [5]. In order to achieve the properties of the final product intended, it is important to choose appropriate textile structures and film-forming materials. Many factors e.g. the possibility of film formation, adhesion, flexibility, and resistance to abrasion, water, solvents, hydrolysis, UV radiation, thermal plasticity, melting, thermal resistance, etc. [6] have an influence on the choice of the basic film-forming polymer. Polyacrylates used to coat textiles are often modified with different functional materials e.g. flame-retardant agents, antistatic, bioactive, UV protection, etc. [7 - 11]. Textile materials made of conventional natural or synthetic fibres may pose a potential fire hazard (eg. in buildings of public use). Conventional polyester such as poly(ethylene terephthalate) (PET) melt and drip tend to degrade and pyrolysis under the influence of the self-sustaining combustion process in fire conditions [7]. This disadvantage limits their use in many areas [1], therefore PET materials are modified with flame retardant agents,

Table 1. *Characteristics of coating pastes; * The amount of thickener Setaprint (PTL) was added to obtain the appropriate viscosity of the paste.*

Paste compositions	Weight percentage, wt%	
	flame-retardants	
	without	with
Dicrylan AC	97.8	54.9
Rustol BXB	0.2	0.1
Pericoat Crosslinker MV	2.0	1.1
Setaprint (PTL)	x*	
Pekoflam TC 303	-	27.4
Pekoflam PES	-	16.5
Viscosity dPas	115	103

Table 2. *Characteristic of fabrics studied.*

Fabric		Raw	With unmodified coating	With flame-retardant coating
Mass per unit area, g/m^2		94	145	218
Mass per unit area of dry coating, g/m^2		-	51	124
The flame retardant content, g/m^2			-	54
Mass per unit area after washing treatment, g/m^2	1 wash		145	185
	5 wash		145	156
	10 wash		145	155
	15 wash		145	156

Table 3. *List of test samples; *R-resin, **f –film.*

Samples	Symbol
Cross-linked polyacrylic resin Dicrylan AC - film	AC/R*/f**
Flame-retardant Pekoflam PES - liquid	FR1
Flame-retardant Pekoflam TC 303 - powder	FR2
Crosslinked coating - film	AC/f
Crosslinked coating with flame-retardants - film	AC/FR/f
Raw PET fabric	PET
PET fabric impregnated before unmodified coating	PET/B1
PET fabric impregnated before flame-retardant coating	PET/B2
PET fabric with unmodified coating	PET/AC
PET fabric with flame-retardant coating	PET/AC/FR
PET fabric with unmodified coating after 1, 5, 10 and 15 washes	PET/AC/1;5;10;15
PET fabric with flame-retardant coating after 1, 5, 10 and 15 washes	PET/AC/FR/1;5;10;15

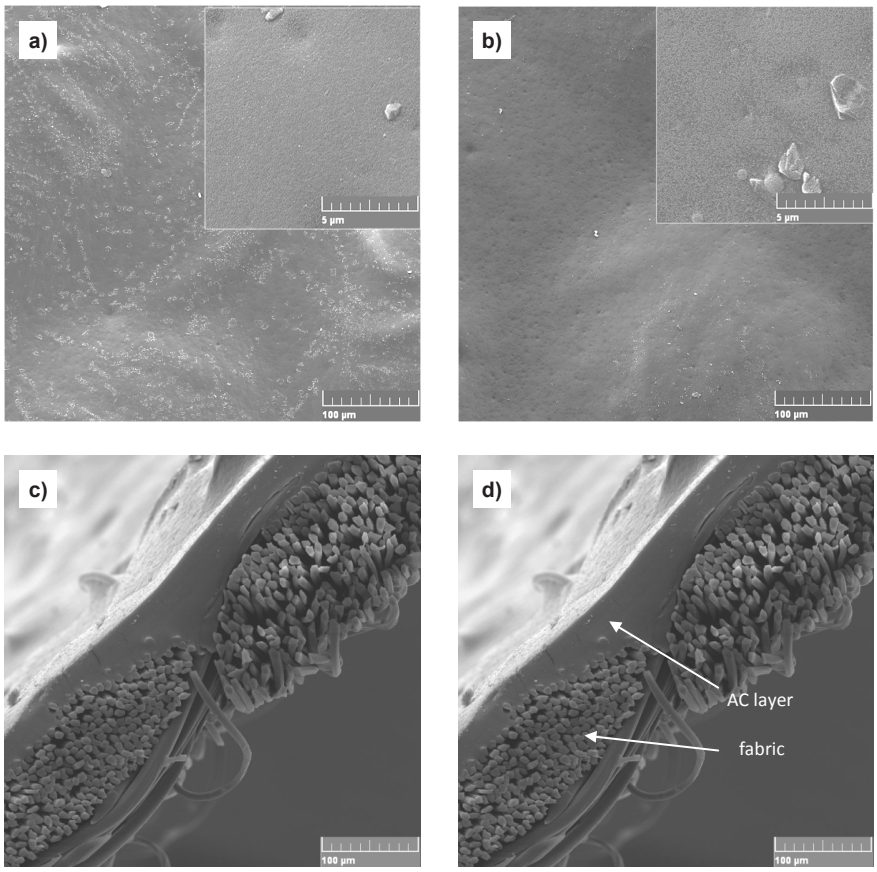

Figure 1. *SEM images of coated fabrics (PET/AC): a) surface of unmodified coating before and b) after 15 washes, c) the cross-section of coated fabric before and d) after 15 washes.*

chosen for raising the temperature of ignition, and for inhibiting or retarding the thermal degradation process of textile materials. For safety reasons, flammability properties should be maintained for the lifetime of the product.

The aim of the study was to assess the thermal properties of polyester (PET) fabrics with unmodified and flame-retardant modified polyacrylate coatings before and after washing treatment. The fabric was modified by a coating technique commonly used, and which met the criteria of flammability tests for curtains. Differential scanning calorimetry DSC andthermogravimetric TG/DTG analyses were carried out in order to investigate the thermal processes. To evaluate the effects of the modifications and washing treatment the scanning electron microscopy SEM/EDS technique was used.

Experimental

Materials

Commercial polyester woven fabric made of poly(ethylene terephthalate) (PET) with a plain weave,warp density of 390/10 cm and weft density of 320/10 cm was used. Before coating with polymer paste without flame retardant agents, the raw fabric was impregnated with a bath (B1) containing 20 g/l Periguard UFC (Dr. Petra, Germany), 3 g/l Periguard EXT (Dr. Petra, Germany), 10 g/l isopropyl alcohol and acetic acid. Before coating with the paste containing flame-retardant agents, the raw fabric was impregnated with a bath (B2) containing 12 g/l Periguard UFC (Dr. Petra, Germany), 100 g/l Pekoflam PES (Clariant, Switzerland), 10 g/l isopropyl alcohol and ammonia.

On the basis of polyacrylic polymer, two types of coating pastes were prepared, with and without flame-retardants (FR) (***Table 1***). For the basic paste, Dicrylan AC (Huntsman, Germany), Rustol BXB (Rudolf, Germany), Pericoat Crosslinker MV (Dr. Petry, Germany), and Setaprint PTL (Setas Kimya) were used, and as flame-retardants Pekoflam TC 303 – inorganic phosphorus compounds and Pekoflam PES – organic phosphorus compounds (Clariant, Switzerland) were applied. The fabric was coated on one side. Characteristics of fabrics studied are presented in ***Table 2***. ***Table 3*** summarizes all of test samples.

Methods

Film preparation

In order to obtain cross-linked films, a thin layer of resin and polymer pastes were poured on Petri dishes and dried in an oven at 110 °C for 4 hours.

Fabric impregnation

Before coating with polyacrylic paste without flame-retardants, the fabric was impregnated on a two-roll padder (Benz, Switzerland, rolles pressure of 3.5 daN/cm) with a bath B1 of 20 °C and dried at 100 °C at a rate of 1.5 m/min for 5 min.

Before coating with flame-retardant modified paste, the fabric was impregnated with a bath B2 of 20 °C (rolles pressure of 3 daN/cm), dried at 100 - 120 - 150 °C at a rate of 1.5 m/min for 3 min, thermal treated at 185 °C for 2 min, and then rinsed in water with 1 g/l Polyacrylic A at 60 °C (2 passages), and next in water at 60 °C (1 passage) and 40 °C (1 passage).

Fabric coating

The fabrics were coated using a coating machine, Werner Mathis AG (Switzerland) with an air knife (distance of 0.1 mm), dried at 100 - 120 °C at a rate of 1 m/min for 10 min and thermal treated at 160 °C for 2 min.

Washing

Samples of coated fabrics were washed in a automatic washing machine - Vascator FOM71 MP LAB (Electrolux, Switzerland) at 40 °C and dried (according to PN-EN ISO 6330: 2012, the program 4N).

Instrumental techniques

SEM/EDS analysis

Microscopic analysis SEM/EDS was carried out using the scanning electron microscope VEGA 3 (Tescan, Czech Republic) with a X-ray microanalyzer - EDS INCA (Oxford Analytical Instruments, UK) at 500× magnification. SEM images, EDS X-ray SmartMaps on a microarea of 46 650 µm^2 and a EDS Sum Spectrum were obtained. The average weight percentage of elements was determined on the basis of the EDS Sum Spectrum obtained for three different microareas of each sample.

DSC analysis

A study of thermal properties was performed using a differential scanning calorimeter -DSC 204 F1 Phoenix (Netzsch,

Germany). All samples were tested in a ceramic crucible with a volume of 85 µl in a nitrogen atmosphere (gas flow of 25 ml/min), at a heating rate 10 °C/min in the range of 20 - 600 °C. Three samples of each material with masses of 5 - 16 mg were examined. Based on the DSC thermograms the melting enthalpy (ΔH_m), the heat of thermal degradation ($\Delta H_{Deg.}$), the initial (T_{Onset}) and final (T_{End}) temperature of melting and the thermal degradation and temperature at the peak maxima (T_{Max}) of the raw and coated fabrics were determined. The initial (T_{Onset}), final (T_{End}) and peak maxima (T_{Max}) temperatures of the thermal degradation and the heat of thermal degradation ($\Delta H_{Deg.}$) of films and flame-retardant agents were determined.

TG/DTG analysis

TG/DTG analysis was performed using a thermogravimetric analyser TG 209 F1 Libra (Netzsch, Germany). All samples were tested in a ceramic crucible with a volume of 85 µl in a nitrogen atmosphere (gas flow of 25 ml/min.), with a heating rate of 10 °C/min in the range of 30 - 600 °C. Three samples of each materials with masses of 5 - 16 mg were examined. The weight loss of samples in the temperature range of peaks occurrence on the DTG curves and the initial (T_{Onset}), final (T_{End}) and the peaks maxima (T_{Max}) temperature of the thermal degradation were determined.

Results and discussion

SEM/EDS analysis

Microscopic images of the coated fabrics are presented in ***Figures 1*** and ***2***. ***Figures 1.a*** and ***1.c*** show the fabric with unmodified coating (PET/AC) before the washing treatment and ***Figures 1.b*** and ***1.d*** - after 15 washes. The coating before washing forms a continuous film with fine pores. After 15 washings (***Figures 1b*** and ***1d***) there were no defects in the coating and pores are clearly smaller. ***Figures 2.a*** and ***2.c*** show the flame-retardant fabric (PET/AC/FR) before the washing with visible agglomerates of flame-retardant agents. After 15 washings (***Figures 2.b*** and ***2.d***) a plurality of recesses/open pores are present, which may be the result of removed flame-retardant agents.

On the basis of X-ray spectra emitted from the flame-retardant agents, it was found that FR1 contains C, O, P and S, and FR2 contains C, N, O & P (***Figure 3***).

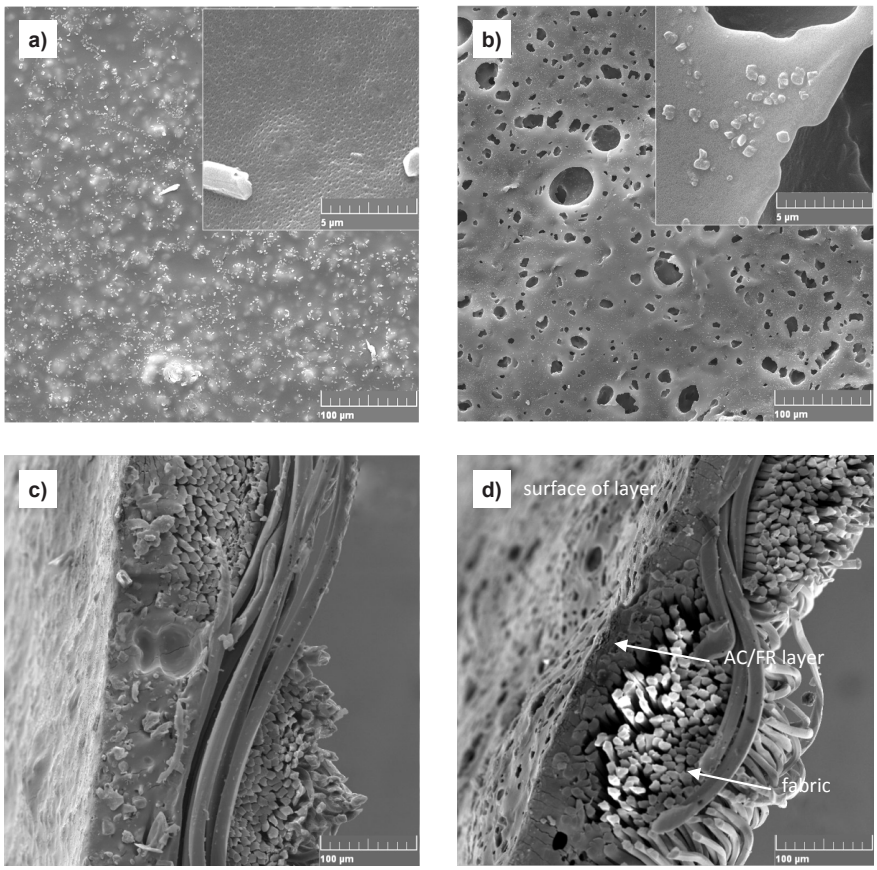

Figure 2. *Figure 2. SEM images of fabrics with flame-retardant coating (PET/AC/FR): a) surface of modified coating before and b) after 15 washes, c) the cross-section of coated fabric before and d) after 15 washes.*

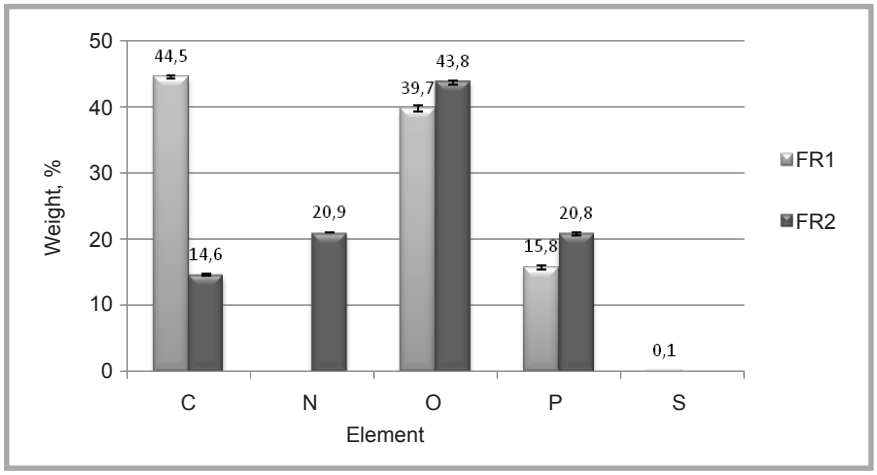

Figure 3. *Weight percentage of elements in flame-retardant agents FR1 and FR2.*

Table 4. *Weight percentage of elements in the flame-retardant coating on the fabric before and after 1, 5, 10 & 15 washes.*

Element	Weight percentage, wt%				
	PET/AC/FR	PET/AC/FR/ 1	PET/AC/FR/ 5	PET/AC/FR/ 10	PET/AC/FR/ 15
C Kα	56.81	64.42	67.95	69.19	67.32
N Kα	3.68	3.31	2.33	1.98	1.74
O Kα	30.59	28.61	27.55	26.79	28.97
Na Kα	-	0.44	1.16	1.32	1.36
P Kα	8.78	3.10	0.90	0.60	0.50
S Kα	0.14	0.11	0.11	0.11	0.10

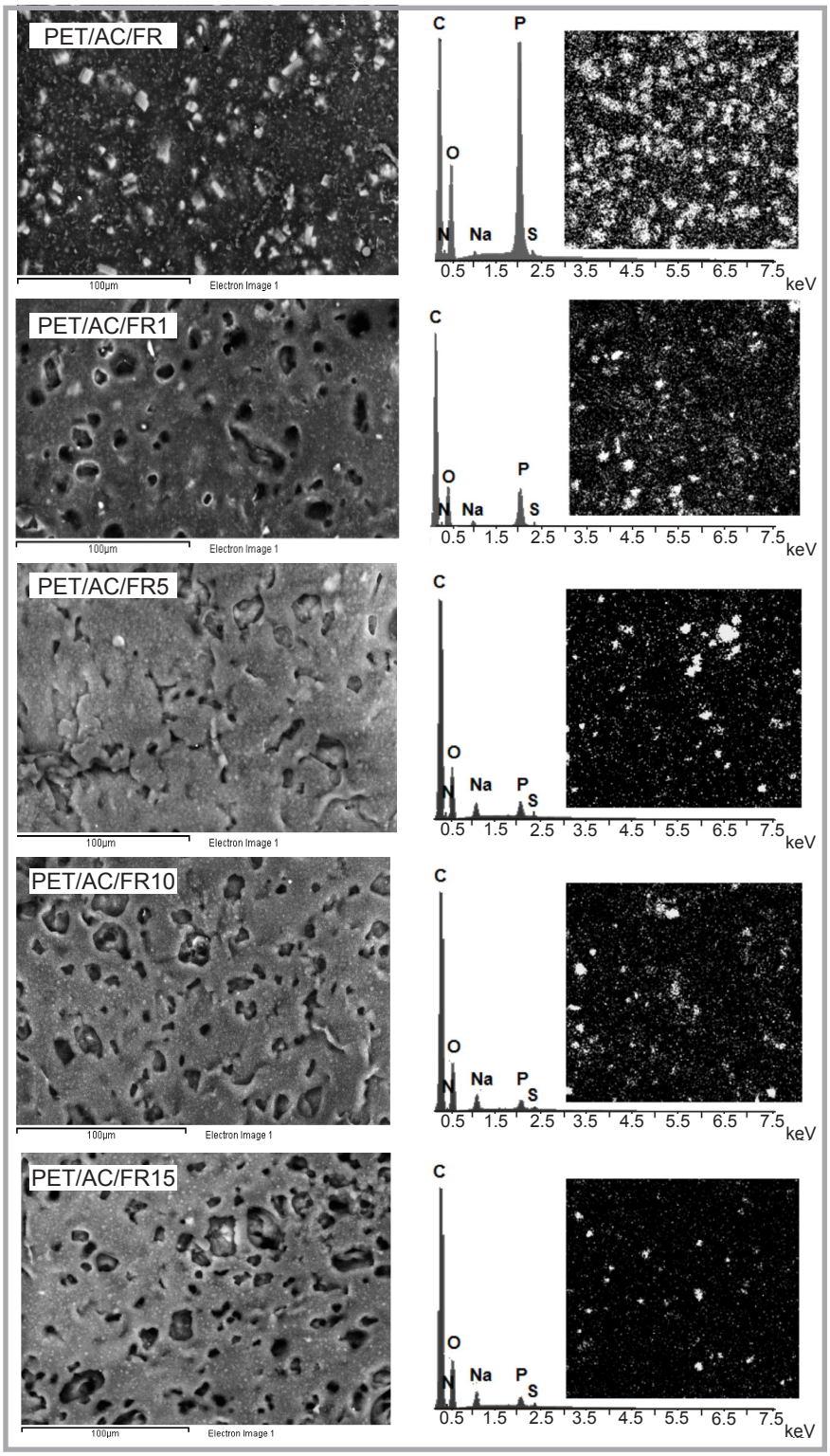

Figure 4. *SEM images, X-ray SmartMaps of phosphorus and Sum Spectra for the flame-retardant coating of fabric before and after the washing treatment.*

Table 5. *Results of DSC analysis for samples studied; [a] mean value ± standard deviation, [b]FR2 thermal degradation process is exothermic; the table shows the absolute value of the heat of its thermal degradation, [c]FR=FR1+FR2 in relation 2:1.*

Sample	ΔH_{Deg}, J/g	T_{Onset}, °C	T_{End}, °C	T_{Max1}, °C	T_{Max2}, °C
AC/R/f	345.8 ± 2.9[a]	375.2 ± 0.4	422.1 ± 1.3	397.3 ± 0.8	-
AC/f	342.6 ± 2.7	365.2 ± 0.7	424.2 ± 0.6	396.4 ± 0.7	-
FR1	562.7 ± 1.1	290.8 ± 1.7	344.9 ± 1.9	326.4 ± 0.8	-
FR2	147.0 ± 2.9[b]	345.3 ± 1.2	352.5 ± 2.1	349.6 ± 0.7	-
AC/FR[c]/f	325.4 ± 2.2	246.1 ± 0.7	402.7 ± 1.0	310.7 ± 1.6	383.7 ± 1.9

FR2 has 20.9 wt% of nitrogen, which is not present in FR1. The percentage of phosphorus is 15.8 wt% and 20.8 wt% in FR1 and FR2, respectively. In FR1 there is also present a small amount of sulphur.

Table 4 shows the weight percentage of elements in the flame-retardant coating on the fabric before and after the washing treatment.

In the coating of PET/AC/FR fabric, C, N, O, P and S were found and the dominant elements are C, O & P. After washing, this coating contains additional Na (0.44 wt% to 1.36 wt%, increasing with the number of washes), which is residue after the washing treatment. The fabric coating with flame-retardants before washing has 8.78 wt% of phosphorus (***Table 4***), derived from FR1 and FR2 agents (***Figure 3***). The proportion of phosphorus in the flame-retardant coating decreases after subsequent washing treatments, from 3.10 wt% to 0.50 wt% (***Table 4***). The flame-retardant agents were rinsed during the washing treatment. Changes in the contents of phosphorus in the fabric coatings obtained by SmartMaps and X-ray spectra confirm the results of SEM image analysis (***Figure 4***).

DSC analysis

In ***Figure 5***, DSC thermograms of all materials and fabrics used are presented. For the raw fabric (***Figure 5.b***) the endothermic melting peak with a maximum at 257.1 ± 0.4 °C (***Table 6***) is visible, and the melting enthalpy is 52.1 ± 0.9 J/g (***Figure 6***). The endothermic peak of thermal degradation reaches the maximum at 442.9 ± 0.9 °C and the heat of thermal degradation amounted to 115.6 ± 0.9 J/g (***Table 6***). A similar result was obtained by Lecomte et al. [12]. Preliminary impregnation of the fabrics before coating with unmodified paste (PET/B1) and flame-retardant paste (PET/B2) does not influence their degradation temperature changes in comparison with the raw fabric. For the impregnated PET/B1 sample an endothermic melting peak with a maximum at 254.9 ± 1.1 °C is present (***Table 6***), and the melting enthalpy amounted to 49.0 ± 1.0 J/g (***Figure 6***). The degradation of the PET/B1 sample takes place in a single step with the endothermic peak maximum at 443.0 ± 1.2 °C and a heat of degradation of 115.5 ± 0.5 J/g (***Table 6***). For the impregnated PET/B2 sample a endothermic melting peak with a maximum at 255.0 ± 1.0 °C is pre-

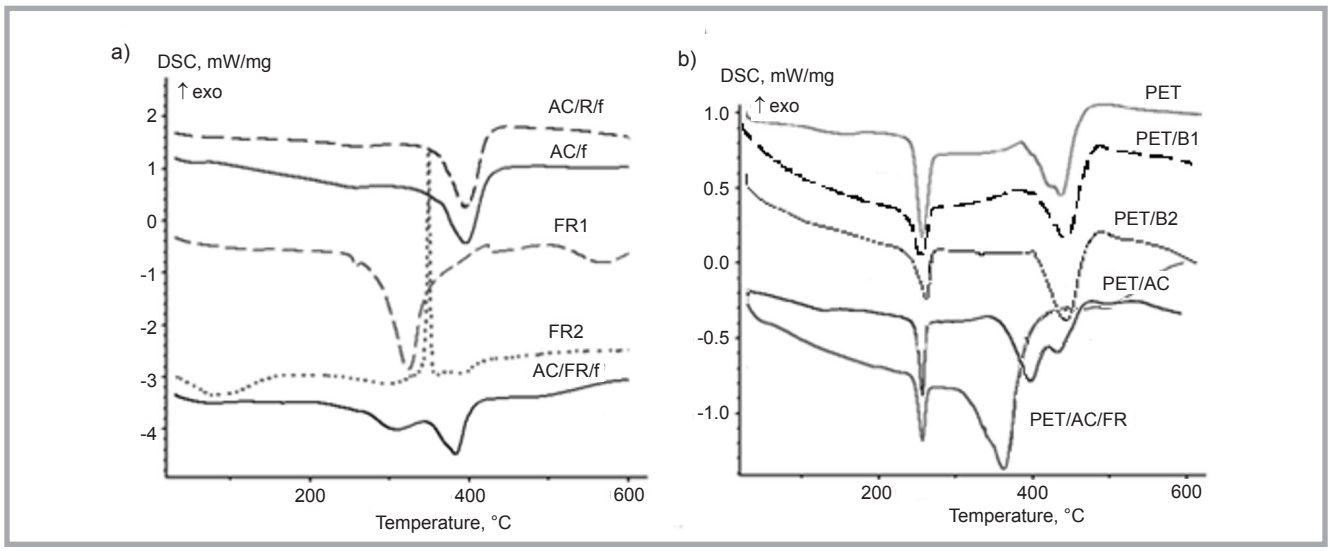

Figure 5. *DSC thermograms of a) cross-linked polyacrylic resin (AC/R/f), cross-linked polyacrylic coating (AC/f), flame-retardant agents (FR1, FR2), cross-linked flame-retardant coating (AC/FR/f), and b) raw fabric (PET), fabric impregnated before unmodified coating (PET/B1), fabric impregnated before flame-retardant coating (PET/B2), fabric with unmodified coating (PET/AC), fabric with flame-retardant coating (PET/AC/FR).*

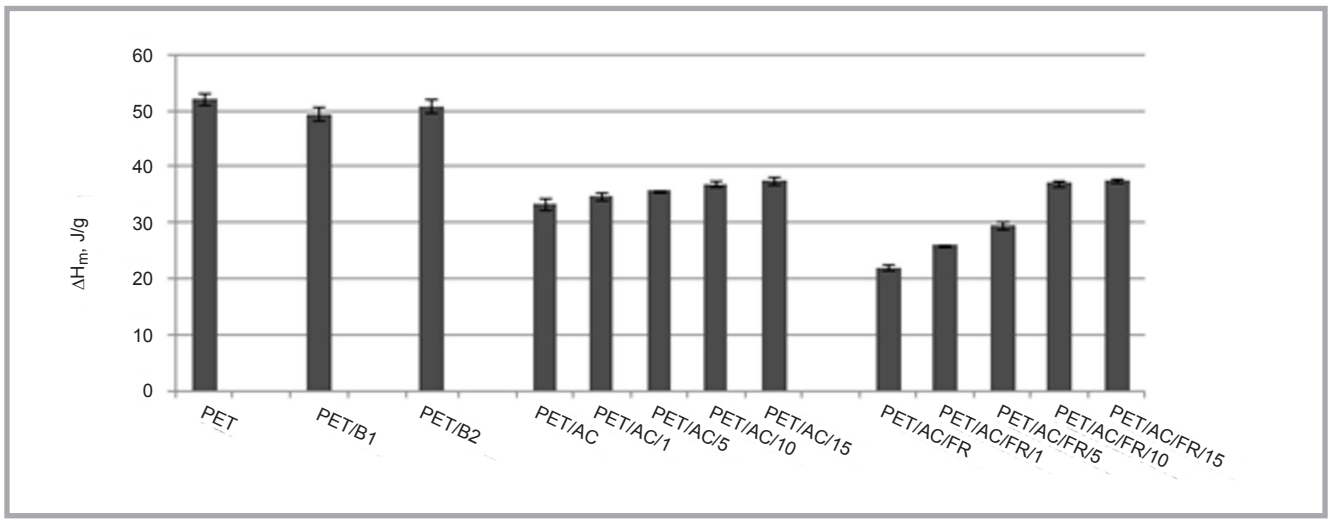

Figure 6. *Melting enthalpy values of fabrics before and after the washing treatment.*

Table 6. *DSC results for fabrics before and after washing treatment; [a]mean value ± standard deviation.*

Sample		Melting process			Thermal degradation process				
		T_{Onset}, °C	T_{End}, °C	T_{Max}, °C	ΔH_{Deg}, J/g	T_{Onset}, °C	T_{End}, °C	T_{Max1}, °C	T_{Max2}, °C
PET		250.9 ± 0.9[a]	261.5 ± 0.7	257.1 ± 0.4	115.6 ± 0.9	403.7 ± 0.7	466.9 ± 0.9	442.9 ± 0.9	-
PET/B1		247.8 ± 0.4	260.7 ± 0.7	254.9 ± 1.1	115.5 ± 0.5	402.9 ± 0.5	465.9 ± 1.3	443.0 ± 1.2	-
PET/B2		249.1 ± 1.0	260.2 ± 0.5	255.0 ± 1.0	115.1 ± 0.7	405.1 ± 0.3	468.1 ± 1.0	444.0 ± 1.0	-
fabric with unmodified coating	PET/AC	251.1 ± 0.3	264.5 ± 0.4	258.7 ± 0.3	198.3 ± 1.5	371.2 ± 1.0	465.2 ± 0.9	398.1 ± 0.7	434.6 ± 0.5
	PET/AC/1	251.4 ± 0.2	265.1 ± 0.3	258.8 ± 0.5	197.5 ± 1.6	363.7 ± 1.1	469.5 ± 0.8	397.3 ± 0.6	434.9 ± 0.8
	PET/AC/5	251.6 ± 0.5	265.4 ± 0.3	259.4 ± 0.4	197.3 ± 1.1	367.2 ± 1.4	470.3 ± 0.5	399.3 ± 1.1	434.9 ± 0.5
	PET/AC/10	251.7 ± 1.8	265.6 ± 1.0	260.0 ± 1.1	195.6 ± 2.1	365.2 ± 0.8	478.2 ± 1.2	397.5 ± 0.2	438.3 ± 0.4
	PET/AC/15	251.6 ± 1.3	265.8 ± 0.3	259.8 ± 0.9	193.9 ± 1.5	364.3 ± 0.9	471.3 ± 1.4	399.0 ± 0.7	438.4 ± 0.8
fabric with flame-retardant coating	PET/AC/FR	249.0 ± 0.5	262.7 ± 0.4	257.7 ± 1.2	242.9 ± 3.0	327.0 ± 2.7	390.3 ± 1.0	362.6 ± 0.6	-
	PET/AC/FR/1	247.2 ± 1.2	262.7 ± 0.9	257.9 ± 1.1	230.8 ± 2.1	344.5 ± 0.8	389.4 ± 0.8	376.6 ± 1.3	-
	PET/AC/FR/5	250.8 ± 0.3	264.8 ± 0.4	259.8 ± 1.0	207.6 ± 2.6	376.4 ± 2.0	472.1 ± 1.0	403.0 ± 1.0	430.4 ± 0.6
	PET/AC/FR/10	250.5 ± 0.6	264.7 ± 1.1	259.8 ± 0.7	207.3 ± 3.2	387.6 ± 1.2	467.5 ± 0.5	403.1 ± 0.5	432.8 ± 0.7
	PET/AC/FR/15	250.3 ± 0.4	263.6 ± 1.3	260.7 ± 0.9	207.6 ± 1.5	380.2 ± 1.6	470.9 ± 0.5	404.8 ± 0.9	437.3 ± 0.4

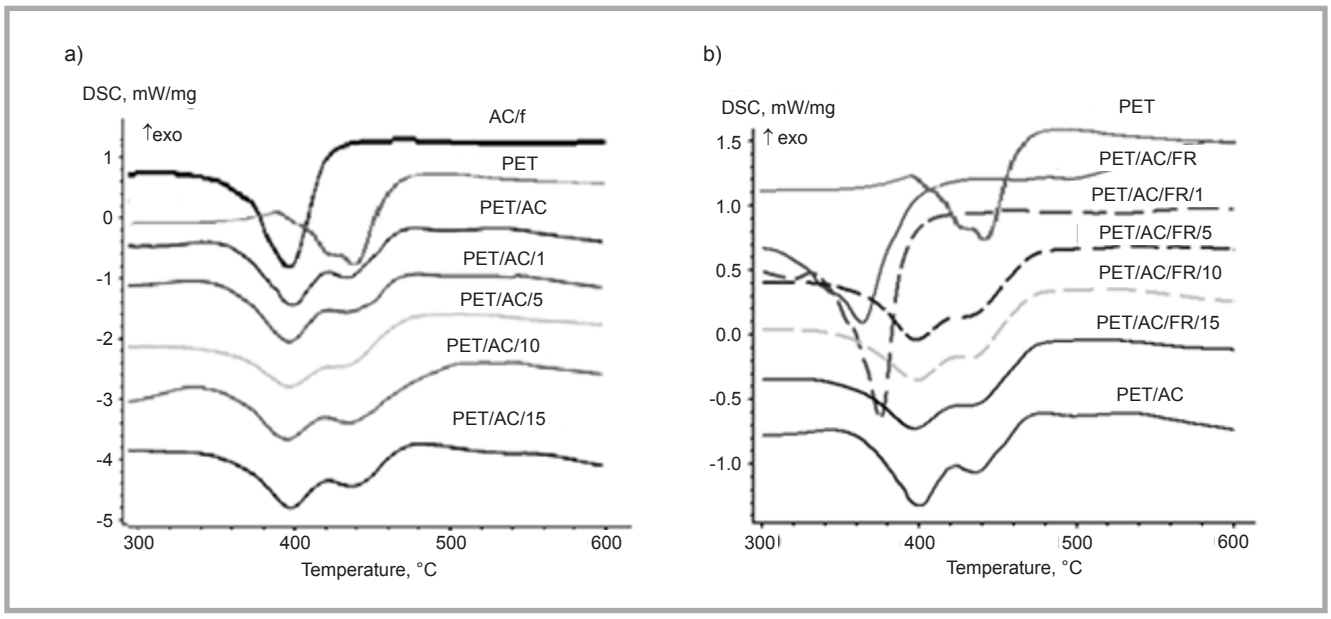

Figure 7. *DSC thermograms of thermal degradation of a) fabrics with unmodified coating and b) fabrics with flame-retardant coating, before and after the washing treatment.*

sent (***Table 6***), and the melting enthalpy amounted to 50.87 ± 1.2 J/g (***Figure 6***). The degradation of this sample takes place in a single step with the endothermic peak maximum at 444.0 ± 1.0 °C and with a heat of degradation of 115.1 ± 0.7 J/g (***Table 6***). Degradation of the cross-linked polyacrylic resin (AC/R/f) takes place in the range of 375.2 ± 0.4 °C - 422.1 ± 1.3 °C with T_{Max1} at 397.3 ± 0.8 °C (***Table 5***) and with a heat of degradation of 345.8 ± 2.9 J/g. Cross-linked polyacrylic coating (AC/f) is degraded in the temperature range of 365.2 ± 0.7 °C - 424.2±0.6°C with T_{Max1} at 396.4 ± 0.7 °C and with a heat of degradation of 342.6 ± 2.7 J/g (***Table 5***). The mass per unit area of PET/AC fabric is 145 g/m^2 (***Table 2***), including raw fabric of mass 94 g/m^2 (65 wt%) and cross-linked coating (AC/f) of mass 51 g/m^2 (35 wt%) (***Table 2***). It can be concluded that the value of thermal degradation heat of PET/AC fabric is the total value of the heat of textile material and coating components. Flame-retardants FR1 and FR2 are degraded at much lower temperatures: FR1 at 290.8 ± 1.7 °C with the endothermic peak at 326.4 ± 0.8 °C and FR2 345.3 ± 1.2 °C with the exothermic peak at 349.6 ± 0.7 °C. Thermal degradation of the cross-linked flame-retardant coating (AC/FR/f) is two-step in the range 246.1 ± 0.7 °C - 402.7 ± 1.0 °C with T_{Max1} at 310.7 ± 1.6 °C and T_{Max2} at 383.7 ± 1.9 °C and with a heat of degradation of 325.4 ± 2.2 J/g (***Table 5***, see page 76).

The unmodified polyacrylic coating causes an increase in the melting temperature T_{Max} of about 1.5 °C (***Figure 5.b***, ***Table 6***, see page 77), a decrease in the melting enthalpy of about 19 J/g (***Figure 6***), and an decrease in the initial temperature of degradation of about 32°C in comparison with the raw fabric. The degradation of unwashed PET/AC fabric takes place in two steps with the endothermic peaks of the textile material and coating (***Table 6***).

The melting temperature T_{Max} of PET/AC/FR fabric decreased by 1 °C in comparison with PET/AC fabric (***Figure 5.b, Table 6***). The melting enthalpy is also lower and amounts to 22.0 ± 0.6 J/g (***Figure 6***). The beginning of thermal degradation occurs at a temperature lower by 44.2 °C. The degradation heat of the PET/AC/FR fabric (***Table 6***), as in the case of PET/AC fabric, is the total value of the heat of two components: the textile material (43 wt%) and cross-linked flame-resistant coating AC/FR/f (57 wt%) (***Table 2***).

As follows from the values shown in ***Table 6***, the washing treatment of PET/AC fabric did not affect changes in the initial temperature of the melting process. The temperature at the maximum of the melting peak increased by about 1 °C. For PET/AC/FR fabric, after 15 washes the initial melting temperature and peak maximum increased, respectively, by 1.3 °C and 3 °C. Multiple washing of PET/AC and PET/AC/FR fabrics caused an increase in their melting enthalpies (***Figure 6***). After 15 washes, the values of the melting enthalpy for PET/AC/15 increased by 4.2 J/g and for PET/AC/FR/15 by 15.6 J/g.

For PET/AC/15 fabric the initial temperature of degradation T_{Onset} decreased by 6.9 °C, and the final temperature T_{End} increased by 5.1 °C (***Table 6***, ***Figure 7.a***). The temperature T_{Max1} and T_{Max2} increased by about 1 °C and 4 °C, respectively, and the value of the decomposition heat decreased by about 4.5 J/g. After the 1st wash the mass per unir area of PET/AC/1 fabric had not changed (***Table 2***). For PET/AC/FR/1 fabric the initial temperature and maximum peak temperature of degradation increased by 17.5 °C and 14 °C, respectively, and the degradation heat decreased by 12 J/g. For both PET/AC/FR and PET/AC/FR1 fabrics, on the DSC thermograms there is no visible characteristic peak of PET component degradation, which indicates that the degradation of PET fabrics occurred simultaneously with the degradation of the flame-resistant coating (***Figure 7.b***). After the 5th wash there is no visible characteristic peak of the flame-resistant coating (***Figure 7.b***), and the mass per unit area of PET/AC/FR/5 (***Table 2***) is reduced by 28%. For this fabric a characteristic peak of the degradation of the unmodified coating is present, which indicates a total or partial flame-retardant rinse, confirmed by the results of the SEM/EDS analysis (***Table 4***). After 5, 10 and 15 washes, characteristic peaks of PET/AC fabric degradation

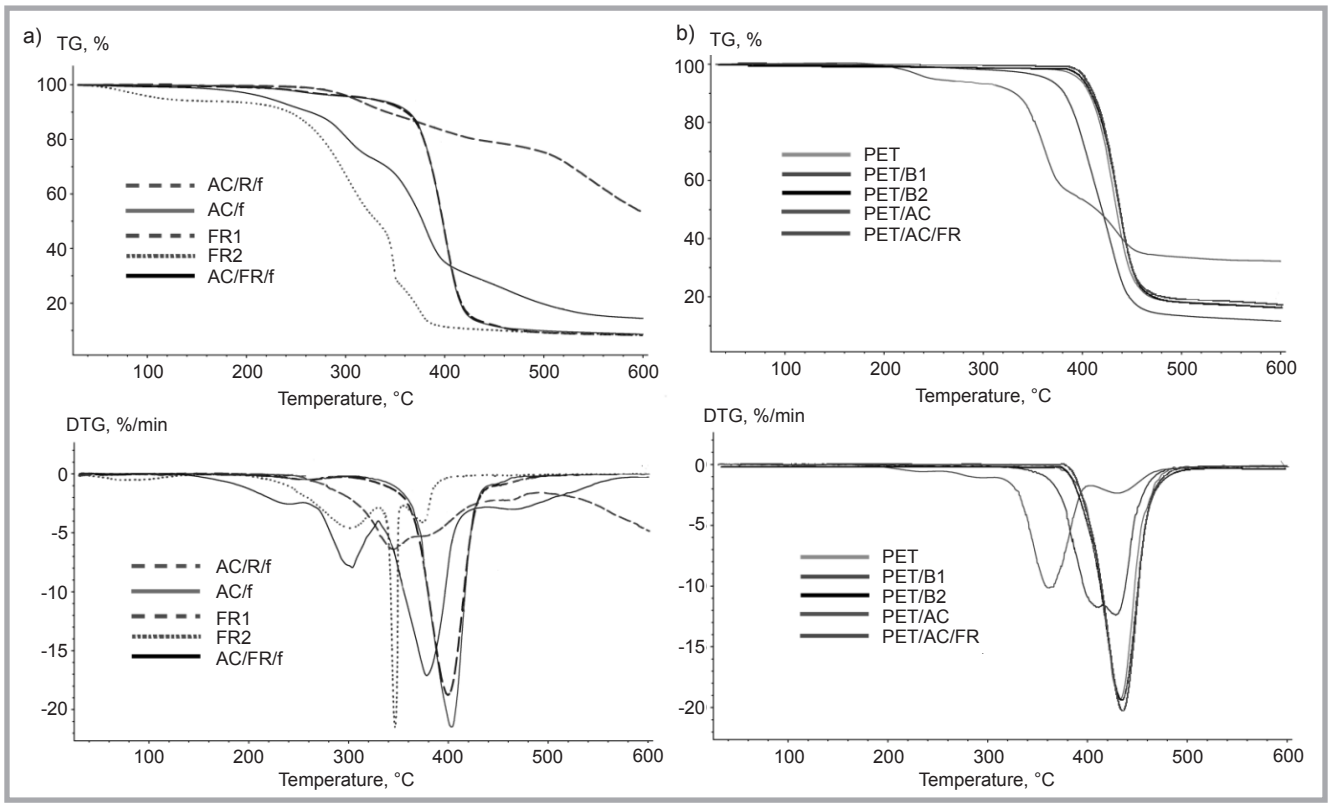

Figure 8. *TG/DTG thermograms of thermal degradation of a) cross-linked polyacrylic resin (AC/R/f), cross-linked polyacrylic coating (AC/f), flame-retardant agents (FR1, FR2), and cross-linked flame-retardant coating (AC/FR/f); b) raw fabric (PET), fabric impregnated before unmodified coating (PET/B1), fabric impregnated before flame-retardant coating (PET/B2), fabric with unmodified coating (PET/AC), and fabric with flame-retardant coating (PET/AC/FR).*

are present. Values of the initial and final temperatures and the endothermic peak maxima of degradation increased and the heat of degradation decreased by 35 J/g compared to the unwashed PET/AC/FR fabric (***Table 6***).

TG/DTG analysis

Thermal degradation of the raw fabric occurs in a single step with T_{Onset} at 395.4 ± 1.1 °C and T_{Max1} 431.1 ± 1.6 °C. A similar result was obtained by Lecomte et al. [12]. The weight loss for the raw fabric at T_{End} 459.8 ± 1.9 °C is 81.3 ± 0.3% (***Table 8***, ***Figure 8.b***). Preliminary impregnations before coating (PET/B1 and PET/B2) did not affect the degradation temperature changes in relation to the raw fabric. Thermal degradation of PET/B1 fabric starts at 396.1 ± 1.8 °C and reaches a maximum of the endothermic peak at 432.7 ± 1.5 °C, and the weight loss at T_{End} 460.8 ± 1.2 °C is 80.2 ± 0.9%. Thermal degradation of PET/B2 fabric starts at 394.9 ± 0.8 °C and reaches a maximum of the endothermic peak at 432.5 ± 0.5 °C, and the weight loss at T_{End} 458.3 ± 0.7 °C is 81.1 ± 0.7%.

Degradation of the cross-linked polyacrylic resin - film (AC/R/f) starts at T_{Onset} 364.4 ± 1.4 °C and proceeds in a single step, with a maximum of the endothermic peak at 406.0 ± 1.2 °C (***Table 7***, ***Figure 8.a***). The process ends at 424.6 ± 1.2 °C with a weight loss of 88.2 ± 1.1%. Similarly, in a single step the cross-linked unmodified coating – film (AC/f) is degraded, with a maximum of the endothermic peak at 401.7 ± 1.1 °C. The process ends at 423.4 ± 0.4 °C, at which the weight loss is 83.4 ± 0.9%.

The degradation of flame-retardant agent FR1 occurs in two steps (***Figure 8.a***):

Table 7. *TG/DTG analysis results for cross-linked polyacrylic resin-film (AC/R/f), cross-linked unmodified coating-film (AC/f), flame-retardants (FR1, FR2), and cross-linked flame-retardant coating-film (AC/FR/f); [b]mean value ± standard deviation.*

		AC/R/f	AC/f	FR1	FR2	AC/FR/f
Step 1	T_{Onset}, °C	364.4 ± 1.4[b]	368.2 ± 0.7	289.2 ± 0.8	245.4 ± 1.4	294.3 ± 2.1
	T_{Max1}, °C	406.0 ± 1.2	401.7 ± 1.1	344.8 ± 0.9	304.0 ± 1.4	296.0 ± 2.5
	T_{End}, °C	424.6 ± 1.2	423.4 ± 0.4	365.2 ± 1.3	332.1 ± 1.2	325.8 ± 2.3
	Residual weight, %	11.8 ± 1.1	16.6 ± 0.9	91.1 ± 0.5	49.4 ± 0.8	80.4 ± 1.2
Step 2	T_{Onset}, °C	-	-	365.2 ± 1.3	332.1 ± 1.2	325.8 ± 2.3
	T_{Max2}, °C	-	-	378.6 ± 0.4	349.5 ± 0.7	382.2 ± 1.8
	T_{End}, °C	-	-	417.9 ± 1.4	357.5 ± 1.1	402.4 ± 1.1
	Residual weight, %	-	-	85.3 ± 0.9	24. 8 ± 0.6	51.5 ± 1.3
Step 3	T_{Onset}, °C	-	-	-	357.5 ± 1.1	-
	T_{Max3}, °C	-	-	-	378.9 ± 0.8	-
	T_{End}, °C	-	-	-	389.0 ± 1.5	-
	Residual weight, %	-	-	-	10.4 ± 1.3	-

Table 8. *TG/DTG results for raw and impregnated fabrics before and after washes.*

		PET	PET/B1	PET/B2
Step 1	T_{Onset}, °C	395.4 ± 1.1[b]	396.1 ± 1.8	394.9 ± 0.8
	T_{Max}, °C	431.1 ± 1.6	432.7 ± 1.5	432.5 ± 0.5
	T_{End}, °C	459.8 ± 1.9	460.8 ± 1.2	458.3 ± 0.7
	Residual weight, %	18.7 ± 0.3	19.8 ± 0.9	18.9 ± 0.7

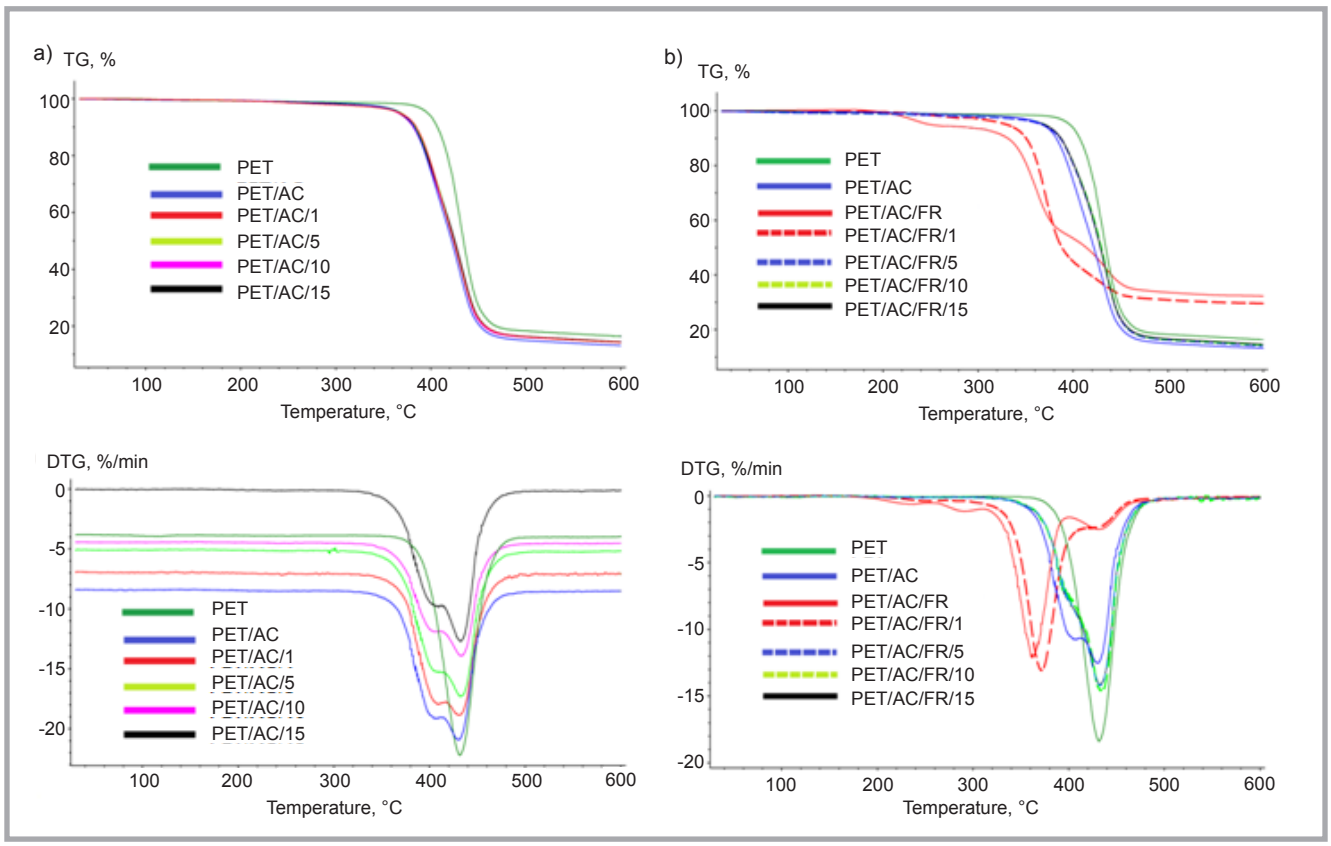

Figure 9. *TG/DTG thermograms of a) fabrics with unmodified coating, and b) fabrics with flame-retardant coating, before and after washes.*

with the beginning at 289.2 ± 0.8 °C and with a weight loss at 600 °C of 27.9 ± 0.8%. For flame-retardant agent FR2 the thermal degradation process proceeds multistage. The weight loss at the final temperature of the third step - 389.0 ± 1.5 °C is 93.5 ± 1.2%. Degradation of the cross-linked flame-retardant coating – film (AC/FR/f) occurs in two steps with a maximum of endothermic peaks at 296.0 ± 2.5 °C and 382.2 ± 1.8 °C. The thermal degradation process ends at 402.4 ± 1.1 °C with a weight loss of 48.5 ± 1.3%.

Table 9. *TG/DTG results for fabrics with unmodified coating before and after washes.*

		PET/AC	PET/AC/1	PET/AC/5	PET/AC/10	PET/AC/15
Step 1	$T_{Onset\ 1}$, °C	376.0 ± 1.1[b]	375.6 ± 0.3	376.8 ± 1.0	374.2 ± 1.1	375.3 ± 0.2
	$T_{Max\ 1}$, °C	405.6 ± 1.4	407.6 ± 1.1	407.7 ± 1.7	405.8 ± 1.0	405.0 ± 0.6
	$T_{End\ 1}$, °C	414.8 ± 0.9	415.7 ± 1.5	415.2 ± 1.0	415.1 ± 0.8	415.7 ± 0.9
	Residual weight, %	59.9 ± 0.3	61.2 ± 0.6	63.6 ± 0.2	66.0 ± 0.7	66.8 ± 0.4
Step 2	$T_{Onset\ 2}$, °C	414.8 ± 0.9	415.7 ± 1.5	415.2 ± 1.0	415.1 ± 0.8	415.7 ± 0.9
	$T_{Max\ 2}$, °C	430.1 ± 0.3	431.4 ± 1.2	431.9 ± 0.3	432.6 ± 1.3	432.0 ± 1.2
	$T_{End\ 2}$, °C	472.4 ± 0.4	476.2 ± 0.5	476.8 ± 2.1	475.4 ± 0.5	474.5 ± 0.9
	Residual weight, %	16.5 ± 0.8	16.5 ± 0.7	16.8 ± 0.0	17.0 ± 0.6	14.8 ± 0.7

Table 10. *TG/DTG results for fabrics with flame-retardant coating before and after washes.*

		PET/AC/FR	PET/AC/ FR/1	PET/AC/ FR/5	PET/AC/ FR/10	PET/AC/ FR/15
Step 1	$T_{Onset\ 1}$, °C	264.8 ± 0.4[b]	343.7 ± 0.5	386.6 ± 0.9	387.7 ± 0.7	386.6 ± 1.2
	$T_{Max\ 1}$, °C	295.3 ± 1.2	372.6 ± 0.9	402.5 ± 0.6	399.3 ± 0.5	398.1 ± 0.7
	$T_{End\ 1}$, °C	311.5 ± 0.9	412.0 ± 1.0	413.4 ± 0.8	410.0 ± 1.2	411.8 ± 1.2
	Residual weight, %	92.9 ± 1.1	71.1 ± 0.7	64.0 ± 1.2	70.3 ± 1.3	68.2 ± 0.4
Step 2	$T_{Onset\ 2}$, °C	311.5 ± 0.9	412.0 ± 1.0	413.4 ± 0.8	410.0 ± 1.2	411.8 ± 1.2
	$T_{Max\ 2}$, °C	360.7 ± 1.0	433.6 ± 0.8	432.2 ± 0.8	433.7 ± 0.9	432.4 ± 0.9
	$T_{End\ 2}$, °C	393.7 ± 0.7	463.0 ± 1.6	461.5 ± 1.3	454.6 ± 0.9	454.1 ± 1.0
	Residual weight, %	54.7 ± 0.8	30.0 ± 0.9	17.5 ± 1.2	17.7 ± 1.4	17.5 ± 1.1
Step 3	$T_{Onset\ 3}$, °C	393.7 ± 0.7	-	-	-	-
	$T_{Max\ 3}$, °C	434.8 ± 1.6	-	-	-	-
	$T_{End\ 3}$, °C	463.3 ± 0.9	-	-	-	-
	Residual weight, %	34.3 ± 0.6	-	-	-	-

The degradation of PET/AC fabric begins at a much lower initial temperature than the raw fabric (***Table 9***, ***Figure 8.b***). This is due to the presence of polyacrylic coating, which degrades faster than the textile component, reducing the initial degradation temperature. A two-stage process begins at 376.0 ± 1.1 °C (***Table 9***), which corresponds to the initial degradation temperature of the polyacrylic unmodified film (AC/f), being higher than the temperature of the cross-linked unmodified coating-film (AC/f) by about 7.8 °C. The peak maximum of this step occurs at 405.6 ± 1.4 °C (about 4 °C higher than T_{Max1} of AC/f). The second step begins at 414.8 ± 0.9 °C and is associated with the initial degradation temperature of PET/AC fabric (***Table 9***), for which the T_{Onset} is higher by 19.4 °C than the temperature for the raw fabric. The peak maximu the T_m of second step T_{Max2} for the PET/AC occurs in 430.1 ± 0.3 °C and is almost comparable to the value of the T_{Max1} for the raw fabric. The weight loss of PET/AC fabric in T_{End} at

472.4 ± 0.4 °C is 83.5%, which is higher by 2.2% than for the raw fabric.

PET/AC/FR fabric is degraded with three steps (***Table 10***, ***Figure 8.b***). The first step begins at 264.8 ± 0.4 °C. The second step is the main step of thermal degradation and corresponds to the degradation of the cross-linked flame-retardant coating. The third step is connected with the degradation of the textile component. For this step the initial temperature is lower by about 1.7 °C, and the temperature T_{Max3} is higher by 3.7 °C than for the raw fabric (***Table 8***). The weight loss at at the end temperature of the last step amounted to 65.7 ± 0.6% (***Table 10***).

The results confirm those obtained by Alongi et al. [7], who observed that the thermal degradation of coated fabric proceeded at a lower temperature with less weight loss than uncoated fabric. The initial temperature of the whole composite degradation was 370 °C, which was lower by 16 °C than for PET fabric. In our work, the difference between the initial temperature for the PET/AC/FR fabric and for the raw fabric is 130.6 °C. The weight loss of uncoated and coated fabrics obtained by Alongi et al. [7] is 90% and 84%, respectively. In our case, the weight loss is 81.3% and 65.7% for the raw PET fabric and coated PET/AC/FR fabric, respectively. The reduced thermal stability of the fabric made of cotton and fireproofed polyester (PESFR/Cotton) with polyacrylic coatings with and without flame-retardants in comparison with raw PESFR/Cotton fabric was also found by Drevelle et al. [11]. The thermal degradation of coated fabrics started at 230 °C and 280 °C, respectively, which aremuch lower than for raw PESFR/Cotton fabric (300 °C). Lefebvre et al. [1], who studied the thermal properties of PETFR/Cotton fabric with polyacrylic coating and raw fabric, did not observe the influence of the coating on thermal degradation temperatures.

In our work the flame-retardants contain phosphorus. It was documented that this element acts in a condensed phase by increasing the amount of char residue, which restricts the release of gases (volatile fuels), melting and further thermal decomposition of the modified coating and modified textile material [7, 10, 11, 13 - 16].

Ten-times washing did not bring about significant changes in the TG/DTG weight loss of PET/AC fabric, which amounted to about 83% (***Table 9***, ***Figure 9.a***). After the 15th wash the weight loss increased by 1.7%; the initial temperature decreased by 0.7 °C; the final temperature increased by 0.9 °C; the temperature at the maximum peak T_{Max1} did not change, and T_{Max2} increased by about 2 °C. In the case of PET/AC/FR fabric after the 1st wash the initial temperature increased by about 78.9 °C and the weight loss increased by 4.3% (***Table 10***, ***Figure 9.b***), which indicates the partial remove of flame-retardants from the coating. After the 5th wash the weight loss increased by 16.8% and the initial temperature by 121.8 °C, similar to the sample after 15 washes (***Table 10***). After 5, 10 and 15 washes the peak characteristic for the flame-retardants is not observed on DTG thermograms, and characteristic peaks of PET/AC fabric degradation are present only (***Figure 9.b***). This indicates that the flame-retardants were already rinsed after the fifth wash, which was also found by the SEM/EDS analysis (***Table 4***, ***Figure 4***).

Conclusions

The aim of the study was to assess the thermal properties of polyester, PET, fabrics with unmodified and flame-retardant modified polyacrylic coatings after washing treatment.

The presence of polyacrylic coating resulted in a decrease in the enthalpy of phase transformation of the coated fabric as compared to the raw fabric. Multiple washing treatment of the coated fabric influenced the melting enthalpy, but the initial melting temperature of the unmodified coated fabric did not vary. Flame-retardant coating resulted in a reduction in the melting enthalpy value. Thermal decomposition starts at a lower temperature than for the unmodified coated fabric, because of the presence of flame-retardant agents. Also the melting process begins at a lower temperature in comparison with the raw fabric. The TG/DTA weight loss of the flame-retardant coated fabric before washing is much lower than for the raw and unmodified coated fabrics. The TG/DTA residual weight for the flame-retardant fabric is significantly higher in comparison to the unmodified coated fabrics corresponding to the mechanism of flame-retardant activity in the condensed phase i.e. increasing the amount of residue, thereby restricting the release of gases and thermal decomposition of the modified textile material. Washing treatment increased the initial melting temperature of the flame-retardant coated fabric. After five washes there are no signs of flame-retardants on the thermograms, which is the result of their having been rinsed out, which confirms the results of SEM/EDS analysis. Polyacrylic coatings cause a decrease in the initial thermal degradation temperature of the whole composite, especially for the flame-retardant version. The flame-retardant modification tested is not resistant to multiple washing. The techniques used may be useful for development and initial assessment of flame-retardant textile materials before testing on a bigger scale, according to suitable flammability tests.

Acknowledgements

- *The study has been carried out within the project BZT 0132 on the apparatus purchased in projects: POIG.01.03.01-00-004/08 Functional nano- and micro textile materials - NANOMITEX co-financed by the European Union with the financial resources of the European Regional Development Fund and the National Centre for Research and Development and WND-RPLD.03.01.00-001/09 co-financed by the European Union with the financial resources of the European Regional Development Fund and the Ministry of Culture and National Heritage*
- *The authors would like to thank Ms D. Kowalczyk, Ms G. Malinowska and Ms A. Kaleta for their technical contribution in the coating process.*

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Received 28.01.2015 Reviewed 02.03.2015