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Structural Changes in the PACVD-Modified Para-Aramid, Ballistic Textiles During the Accelerated Ageing

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Abstract

The process of textile modification using Plasma Assisted Chemical Vapour Deposition (PACVD) results in significant changes in surface properties with high effectivity. However, the main problem of the above-mentioned modification is to obtain a stable modification effect during standard use and storage. The aim of the study was to determine the stability of structural properties of PACVD-modified para-aramid ballistic woven fabrics during accelerated ageing using temperature or simultaneously temperature and humidity as the accelerated ageing factors. For identification of potential changes in the textile surface modified by PACVD with deposition of the polymer formed based on tetradecafluorohexane, the ATR-FTIR and SEM/EDS techniques were applied. The PACVD-modified textiles showed insignificant changes in structural properties after accelerated ageing using the above-mentioned ageing factors. This confirms the stability of the PACVD-resulted modification during simulated conditions of standard use.

Introduction

The idea of prolongation of the safe use of ballistic protectors made on the basis of textile materials (both using HMWPE or p-aramid fibres) has been the main focus of several studies [1, 2].

The effect of accelerated ageing on the main physico-mechanical properties was tested in [3] using PACVD-modified soft UHMWPE fibrous composite fabrics with deposition of a silane-like-polymer onto their surface. The process of PACVD-modification was carried out as described in [4]. The accelerated ageing of PACVD-modified UHMWPE composites confirmed the significant effect of the surface-deposited polymer on the main performance of the ballistic textile and protection influence against the ageing factors. Moreover the results obtained varied due to the type of accelerated ageing factor used.

The accelerated ageing of p-aramid woven fabrics modified by PACVD with the deposition of fluoropolymer in similar conditions yielded the induction of superhydrophobic behaviour of the textile, which affected the resistance against destructive ageing factors [5].

Taking the above into account, the main interest is to find any correlation between the ageing conditions and potential changes in the structure of PACVD-modified textiles. There are some possible interactions between the newly formed layers of the polymer deposited and the protection effect during accelerated ageing.

The aim of the study was to determine the stability of structural properties of PACVD-modified para-aramid ballistic woven fabrics during accelerated ageing using temperature or simultaneously temperature and humidity as the accelerated ageing factors.

Materials

Textile materials

Woven fabric Style 363/120 (SAATI S.P.A, Italy) made of p-aramid yarns was used during the study. The main properties of the textile used are listed in ***Table 1***.

Substrates for PACVD (Plasma Assisted Chemical Vapour Deposition)

For surface PACVD modification of selected textile materials, tetradecafluorohexane; $CF_3(CF_2)_4CF_3$; (TDFH),

Table 1. *Characterization of Style 363/120 woven fabric used in the study [3, 4, 7].*

Surface mass, g/m^2	Thickness, mm	Tensile strength, N		Elongation at the maximum force, %		Bursting strength
		warp	weft	warp	weft	
PN-ISO 3801:1993	PN-EN ISO 5084:1999	PN-EN ISO 13934-1:2002				PN-EN 863:1999
212±2	0.20±0.02	6700±200	6800±500	7.0	5.1	79±10

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99%, Tokyo Chemical Industry/Japan was used.

Methods

Surface modification of textile materials by PACVD

Modification of textile materials (the substrates) in glow discharges was performed in a commercial plasma jet – CD 400PLC ROLL CASSETTE (EUROPLASMA/Belgium) according to [4].

PACVD modified p-aramid Style 363/120 woven fabric was made using the following processing parameters: polymerisation in a stream of tetradecafluorohexane at a flow rate of 0.032 Pa m^3 s^{-1} – 0.064 Pa m^3 s^{-1}with power applied to the electrodes of 200 W, over a time period of 1 min.

Accelerated ageing

The process of accelerated ageing of the modified and unmodified materials was carried out in an ageing system based on TK 720 apparatus (BINDER GmbH/Germany) for thermal ageing at 70.0 ± 0.5°C and the lowest possible relative humidity of 15.0 ± 1.5%. Due to the low humidity of the test environment, the temperature was considered the main accelerated ageing agent.

The second accelerated ageing process was carried out on KBF 240 apparatus (BINDER GmbH/Germany) at a temperature of 70.0 ± 0.5°C and relative humidity of 65.0 ± 1.5% [3,5].

The periods of ageing were established based upon the experience of [6] for 28, 35 or 42 days.

Analytical methods

ATR-FTIR

Tests were performed with a single beam spectrophotometer – FTIR–Nicolet 6700 (THERMO Scientific) according to the method described in [7].

Morphological studies with elemental microanalysis of the chemical composition using the SEM/EDS technique

Chemical and morphological analyses were carried out by means of a scanning electron microscope (SEM) – Nova NanoSEM 230 from FEI company (SE Detector, High Voltage: 10 kV, Low Vacuum) with an X-ray microanalyser – EDS (Energy-dispersive X-ray Spectroscopy) from EDAX (Detector SDD, energy resolution: Mn 132 eV) as described in [7].

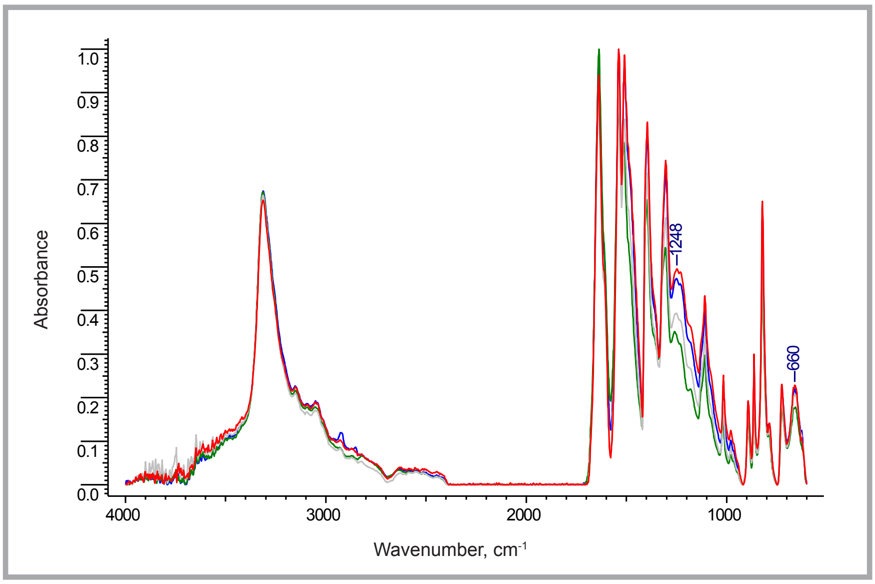


Figure 1. *ATR-FTIR spectrum of unmodified p-aramid fabrics before and after the process of accelerated ageing with the temperature ageing factor: — initial, — after 28 days of accelerated ageing, — after 35 days of accelerated ageing, — after 42 days of accelerated ageing.*

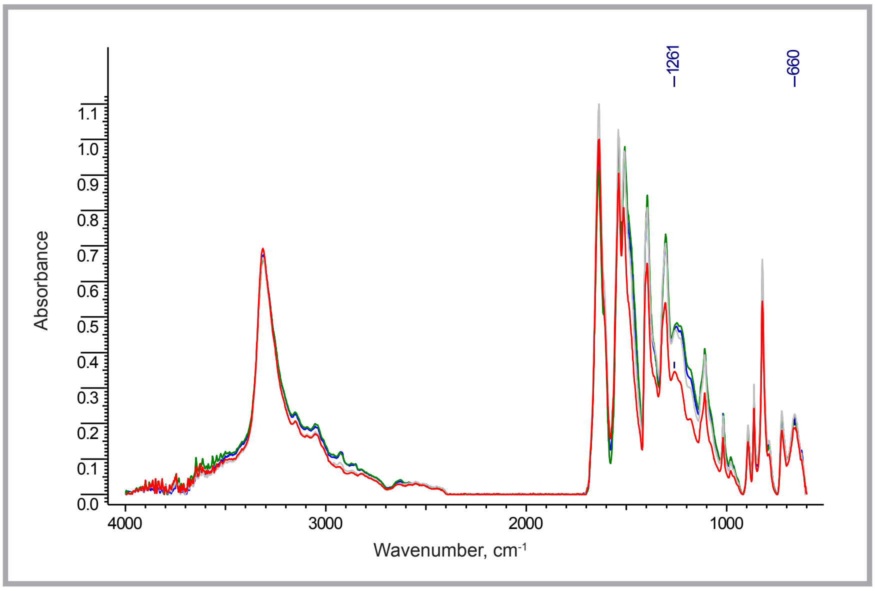


Figure 2. *ATR-FTIR spectra of PACVD-modified p-aramid fabrics before and after the process of accelerated ageing with the temperature ageing factor: — initial, — after 28 days of accelerated ageing, — after 35 days of accelerated ageing, — after 42 days of accelerated ageing.*

Results and discussion

ATR-FTIR analysis

ATR-FTIR spectra of the samples of fabrics unmodified by PACVD and subjected to the process of accelerated ageing with the temperature agent are compared with the ATR-FTIR spectrum of the initial p-aramid ballistic woven fabric in ***Figure 1***.

The process of accelerated ageing of unmodified fabrics performed with temperature as the ageing factor caused an absorption band shift at λ = 1308 cm^{-1} (the C-N bond) towards the lower wavenumbers (1315 cm^{-1}) along with a reduction in the absorption for samples subjected to accelerated ageing for 28 and 35 days. Moreover a minor shift was observed in the wavenumbers at λ = 3064 cm^{-1}, λ = 2920 cm^{-1} (CH) as well as at λ = 1649 cm^{-1}, followed by the formation of a sharp absorption band

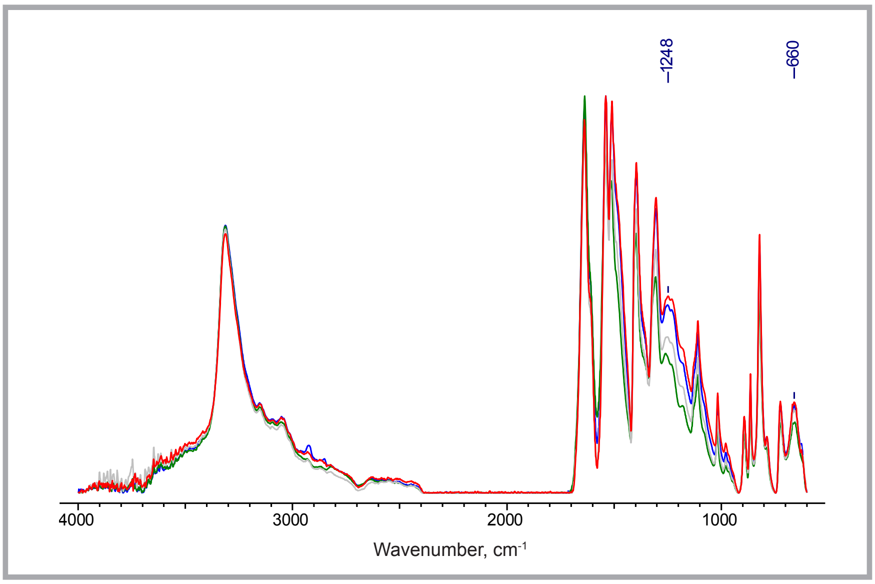


Figure 3. *ATR-FTIR spectra of unmodified p-aramid fabrics before and after the process of accelerated ageing with the temperature and humidity ageing factors: —— initial, —— after 28 days of accelerated ageing, —— after 35 days of accelerated ageing, —— after 42 days of accelerated ageing.*

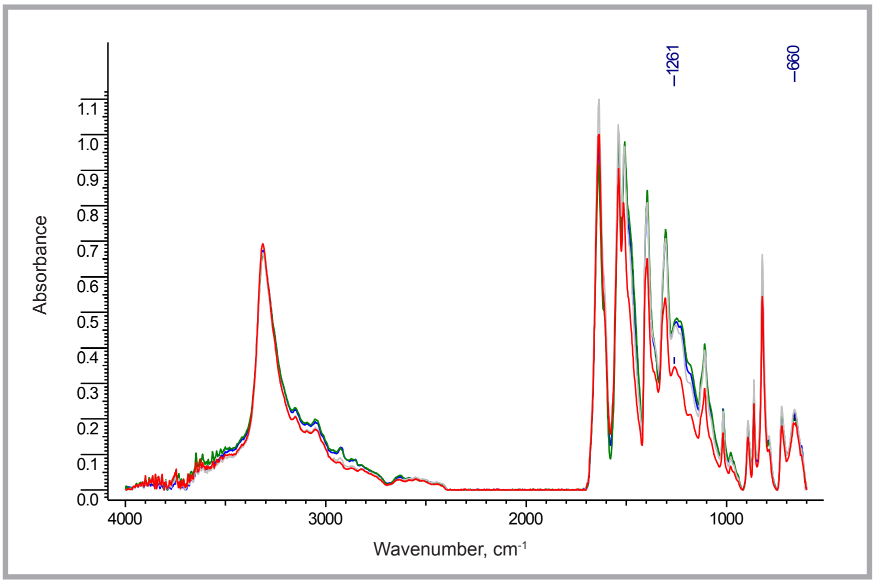


Figure 4. *ATR-FTIR spectra of PACVD-modified p-aramid fabrics before and after the process of accelerated ageing with the temperature and humidity ageing factors: —— initial, —— after 28 days of accelerated ageing, —— after 35 days of accelerated ageing, —— after 42 days of accelerated ageing.*

at λ = 1630 cm^{-1} (CO) for samples after 35 days of accelerated ageing. In FTIR spectra of samples aged for 28 – 35 days a decrease in the absorption band at λ = 1235 cm^{-1} (CH in the para – position of the ring) was also observed.

ATR-FTIR spectra of the fabrics PACVD-modified in the presence of TDFH vapours and subjected to accelerated ageing using the temperature ageing factor are compared to the initial material in ***Figure 2*** (see page 37).

In the ATR-FTIR spectra of PACVD-modified fabrics before and after the accelerated ageing process, absorption bands were observed at λ = 240 cm^{-1} and λ = 1205 cm^{-1} originating from the fluorine-organic substrate. Moreover a shift in the absorption band at λ = 1448 cm^{-1} towards the lower wavenumbers (λ = 1461 cm^{-1}) was found. After 45 days of accelerated ageing a minor reduction in absorption at the above-mentioned wavenumbers was observed. This phenomenon confirms the relatively long-term stability of the ageing process of the modified fabric surface. The durability of fluorine deposition originating from TDFH was affirmed. The process of accelerated ageing performed with the temperature agent does not cause changes in the deposition layer.

ATR-FTIR spectra of PACVD-unmodified fabrics subjected to the process of accelerated ageing with simultaneously acting temperature and humidity ageing factors are compared to those of the initial material in ***Figure 3***.

The process of accelerated ageing of PACVD-unmodified fabrics with the presence of temperature and humidity factors caused a minor shift in absorption bands at wavenumbers λ = 3064 cm^{-1} and λ = 2920 cm^{-1} (CH) as well as at λ = 1649 cm^{-1}, followed by the formation of a sharp peak at λ = 1630 cm^{-1} (CO) after 28 days of the accelerated ageing process. A decrease in the absorption band was observed at λ = 1235 cm^{-1} (CH in the para position of the ring) in ATR-FTIR spectra of material subjected to accelerated ageing for 28 – 35 days.

Figure 4 shows the ATR-FTIR spectra of fabrics modified with PACVD in the presence of TDFH vapours and subjected to the process of accelerated ageing with simultaneously acting temperature and humidity agents in comparison with the ATR-FTIR spectrum of the initial material.

In the ATR-FTIR spectra of fabrics modified with PACVD in the presence of TDFH vapours after the process of accelerated ageing, clear absorption bands were observed at λ = 1240 cm^{-1} and λ = 1205 cm^{-1} originating from the fluorine-organic substrate. These bands were smoothed. Moreover the presence of an absorption band at λ = 1261 cm^{-1} was observed, particularly clear in the samples subjected to the process of accelerated ageing for 42 days. The phenomenon confirms the stability of woven fabric surface modification in a relatively long term process of ageing that applies humidity and temperature as the ageing factors.

The durability of fluorine depositions originating from TDFH was affirmed. The process of accelerated ageing performed with temperature and humidity agents did not cause significant alterations in the deposition layer.

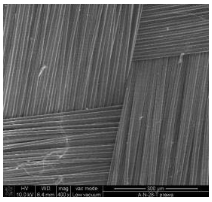
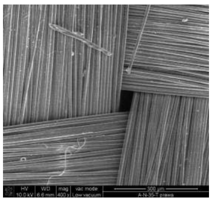
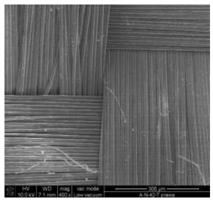
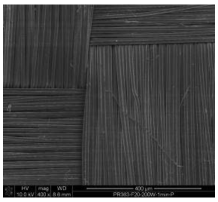
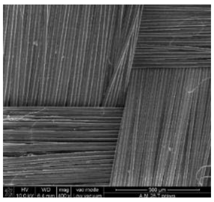
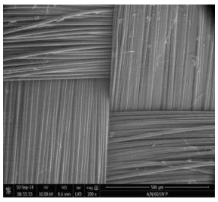
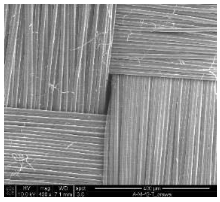
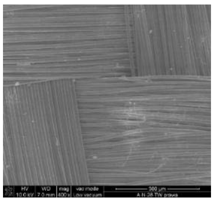
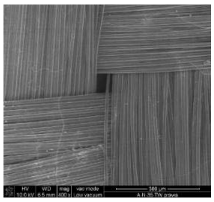
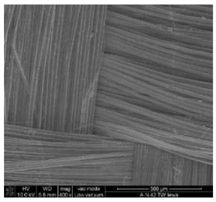
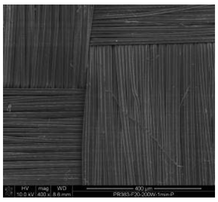
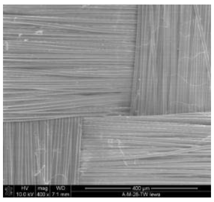
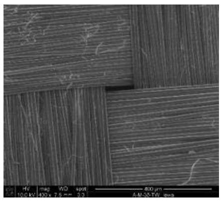
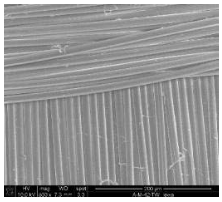
Unmodified p-aramid woven fabric				
	Initial (x800)	Subjected to accelerated ageing for 28 days using temperature factor (x400)	Subjected to accelerated ageing for 35 days using temperature factor (x400)	Subjected to accelerated ageing for 42 days using temperature factor (x400)
PACVD-modified p-aramid woven fabric				
	Initial (x400)	Subjected to accelerated ageing for 28 days using temperature and humidity factors (x400)	Subjected to accelerated ageing for 35 days using temperature and humidity factors (x400)	Subjected to accelerated ageing for 42 days using temperature and humidity factors (x400)
Unmodified p-aramid woven fabric				
	Initial (x800)	Subjected to accelerated ageing for 28 days using temperature factor (x400)	Subjected to accelerated ageing for 35 days using temperature factor (x400)	Subjected to accelerated ageing for 42 days using temperature factor (x400)
PACVD-modified p-aramid woven fabric				
	Initial (x400)	Subjected to accelerated ageing for 28 days using temperature and humidity factors (x400)	Subjected to accelerated ageing for 35 days using temperature and humidity factors (x400)	Subjected to accelerated ageing for 42 days using temperature and humidity factors (x400)

Figure 5. *SEM microphotographs of p-aramid woven fabrics, initial and subjected to accelerated ageing.*

SEM-EDS analysis

The surface topography of the woven materials, both the initial and that subjected to accelerated ageing, is shown in ***Figure 5***.

The structure of the unmodified fabrics and their single fibres did not undergo significant changes during the process of accelerated ageing using temperature – it was smooth, without obvious defects. Single fibres were locally covered with an amorphous substance – apparently textile finishing-aids.

PACVD-modification of the textile resulted, as in the unmodified fabrics, in the absence of significant changes in the structure of the fabrics and fibres during the process of accelerated ageing. Single fibres were locally covered with an amorphous substance – apparently the textile finishing-aids. However, a significantly lower amount of those amorphous substances was found on the surface.

If temperature and humidity were used as the ageing factors, the structure of the unmodified fabrics and fibres did not undergo significant changes in the process of accelerated ageing. It was smooth, without obvious defects, as observed in accelerated ageing with the temperature factor. Single fibres were locally covered with an amorphous substance – apparently textile finishing-aids.

The structure of PACVD-modified fabrics and fibres, as in the unmodified

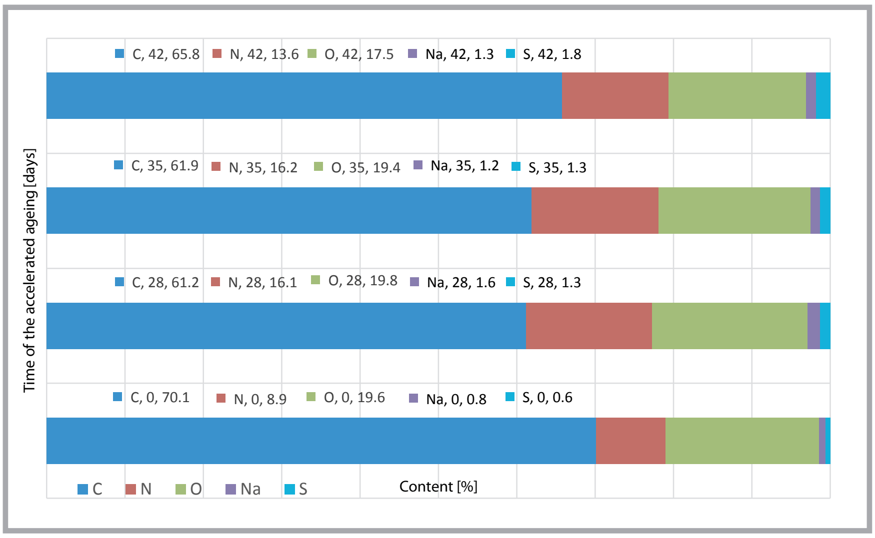


Figure 6. *Surface composition [%] of the initial, unmodified p-aramid woven fabrics, and those subjected to the accelerated ageing process with the temperature ageing factor.*

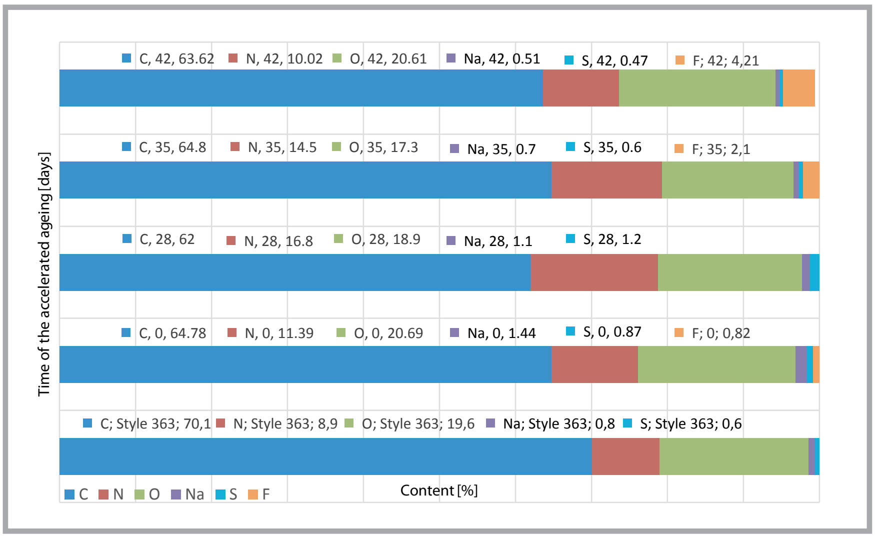


Figure 7. *Surface composition [%] of the initial, PACVD-modified p-aramid woven fabrics, and those subjected to the accelerated ageing process with the temperature ageing factor.*

ones, did not undergo significant macro- nor microscopic changes in the process of accelerated ageing – it was smooth and free of obvious defects. In the PACVD-modified fabrics a significantly lower amount of amorphous substances was found (visible only on the surface of single fibres).

Figure 6 below contains a thorough SEM-EDS analysis of unmodified p-aramid woven fabrics subjected to the process of accelerated ageing with a temperature agent.

The presence of traces of sulphur and sodium was found in the samples, also visible in the initial fabric, probably coming from textile finishing-aids.

An increase in the presence of nitrogen on the surface of the textile at the expense of carbon was observed during accelerated ageing using temperature. The oxygen content remained at a similar level, with the exception of the sample aged for 42 days, in which a slight decrease was found.

The composition of PACVD-modified textile during accelerated ageing using temperature as the ageing factor is show in ***Figure*** *7*.

The presence of traces of sulphur and sodium was found in the samples, also visible in the initial fabric, probably coming from textile finishing-aids. The increasing presence of nitrogen on the surface of the fabric was observed during the accelerated ageing process, compared to the initial, unmodified sample, at the expense of carbon. The oxygen content remained at a similar level during the accelerated ageing study. An increase in fluorine content in the sample surface was observed (from the initial 0.82% to 4.21% after 42 days of accelerated ageing), which may be linked with the effect of surface smoothing under the impact of temperature during the accelerated ageing.

Figure 8 shows changes in the composition of unmodified p-aramid fabrics during accelerated ageing when temperature and humidity were applied.

During the accelerated ageing process, the increasing presence of nitrogen on the surface of the unmodified textiles was observed at the expense of carbon, similarly as in the samples of initial unmodified fabrics aged with the temperature agent only. The oxygen content slightly increased after the first stage of accelerated ageing (28 days) and then remained at a similar level when the ageing process continued. Moreover traces of sulphur and sodium were detected in the samples, also visible in the initial fabric, probably coming from textile finishing-aids.

Changes in the surface compositions of PACVD-modified p-aramid woven textiles subjected to accelerated ageing with temperature and humidity applied as the ageing factors are shown in ***Figure 9***.

The process of accelerated ageing carried out with temperature and humidity caused an increase in nitrogen presence on the surface after 28 days of ageing (similar to the phenomena detected for the ageing of the unmodified sample at the same ageing conditions), at the expense of the carbon content, with the content of oxygen remaining at a similar level. An increase in fluorine content was observed on the surface of the fabrics during the accelerated ageing process. The above phenomenon was similar to that detected for the process performed with a temperature agent and may be linked with the effect of smoothing the textile surface under the impact of a temperature agent only. Moreover, similar to ageing with temperature, traces of sulphur and sodium were found. Additionally traces of chlorine were identified locally, probably originating from the textile finishing-aids.

Conclusions

In the research a wide range of verifications were carried out for structural changes during the accelerated ageing process occurring in (fluoropolymer) layers deposited with the PACVD process onto p-aramid fabric, which were then compared to the initial, unmodified textiles that had not undergone the accelerated ageing process. Based on ATR-FTIR and SEM-EDS studies, the presence of a stable fluoropolymer layer was found after the process of accelerated ageing when aged with the following ageing factors: temperature or temperature with humidity.

No significant changes in the morphology of the topography of the materials examined were found, subjected or not to the process of treatment with PACVD in the presence of TDFH vapours.

The process of accelerated ageing, especially carried out on materials modified with PACVD in the presence of a substrate of fluorine-organic vapours led to an increase in the amount of fluorine on the surface of the textile materials. This phenomenon is probably related to partial, low-particle degradation, smoothing of the surface and quasi migration of fluoropolymer to the surface of the textiles, allowing better detection with the EDS and ATR-FTIR methods.

Structural changes occurring in the textile materials subjected or not to the process of treatment with PACVD in the presence of fluorine-organic substrates under the impact of the accelerated ageing process were directly determined by the ageing agent applied.

As a result of the study, a relatively high resistance was confirmed of fluoropolymer layers deposited with low temperature plasma, in conditions of the accelerated ageing, performed with the temperature or temperature and humidity ageing factors.

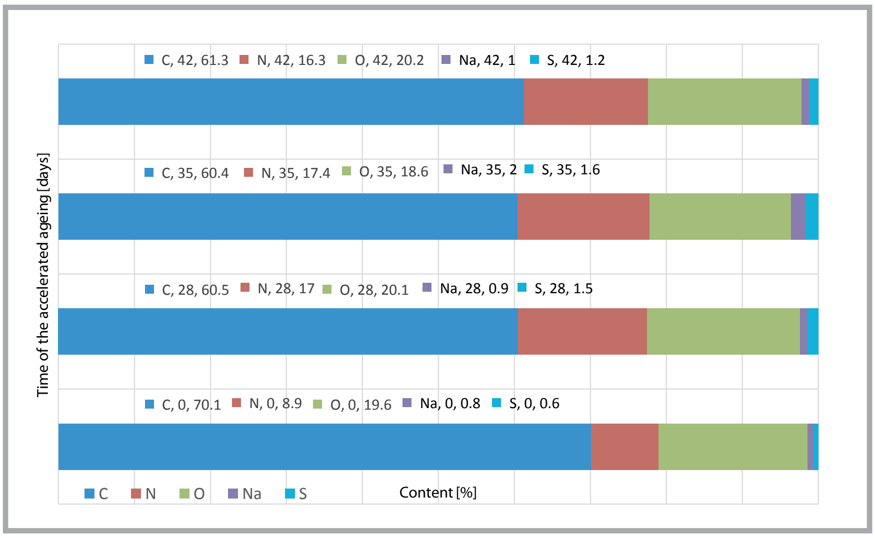


Figure 8. *Surface composition [%] of the initial, unmodified p-aramid woven fabrics, and those subjected to the accelerated ageing process with the temperature and humidity ageing factors.*

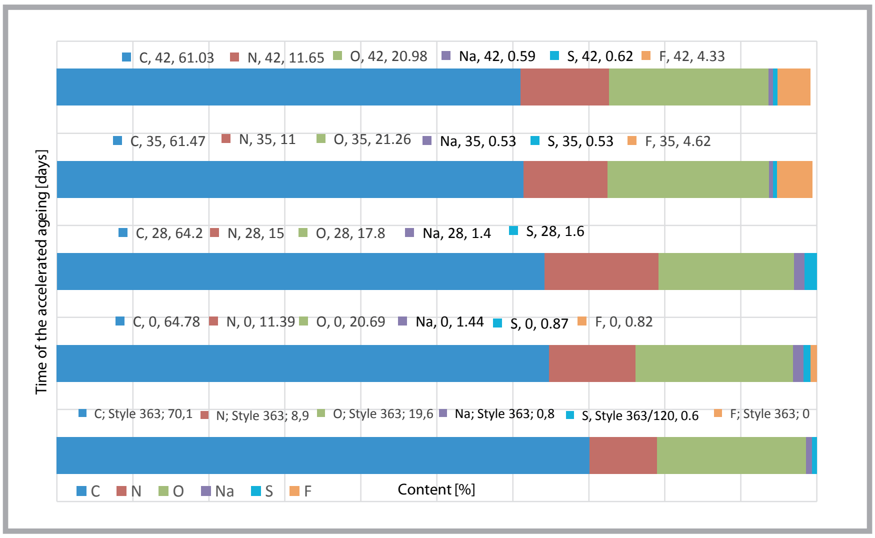


Figure 9. *Surface composition [%] of the initial, PACVD-modified p-aramid woven fabrics, and those subjected to the accelerated ageing process with the temperature and humidity ageing factors.*

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