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Performance Stability of Ballistic Para-Aramid Woven Fabrics Modified by Plasma-Assisted Chemical Vapour Deposition (PACVD)

DOI: 10.5604/12303666.1201137

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Abstract
Plasma-assisted chemical vapour deposition (PACVD) is often used for the modification of the surface properties of a wide range of materials. The resulting effect of PACVD modification considerably changes the behaviour of the material. The process of surface modification by PACVD of a textile is significantly complex due to the topography resulting in the fabric structure. Taking ecology and economy into account, PACVD modification is more efficient as compared with traditional finishing processes. However, the stability of the PACVD effect gets lost during usage of the textile under standard conditions. The aim of the research was to verify in an enhanced accelerated ageing test the stability of PACVD modification of para-aramid woven fabrics applied for designing of soft ballistic inserts in body protectors. The simulated ageing yielded a significant change in the mechanical properties of non-modified textiles, whereas PACVD-modified samples showed prolonged stability of the properties obtained.

Key words: *para-aramid ballistic woven fabrics, PACVD, accelerated ageing.*

Introduction

Plasma-assisted chemical vapour deposition (PACVD), compared to the traditional finishing techniques of textile, has shown a wide range of advantages: high process efficiency as welll as reduction of water use, pollution emission to the environment and energy consumption [1]. Taking the above into account, the PACVD process allows for the introduction of critical changes in high-tech textiles suitable for special application, incl. ballistic protectors.

Two types of fibrous materials are applicable for the design of soft inserts in ballistic protectors: woven fabrics made of para-aramid yarns and a fibrous sheet of oriented fibres of ultrahigh molecular weight polyethylene.

The most important feature of ballistic protectors is to keep the performance and safety during storage and usage. Body protectors are usually used in critical conditions I.e. at relatively high temperature (due to thermal insulation) and high humidity (external conditions and/or user sweating). The above conditions may lead to the degradation of para-aramid, resulting in a reasonably quick loss of ballistic performance of the final product. Considering the above, it is important to find relatively cheap and environmental-friendly techniques for the preservation of ballistic fabrics against external factors in order to guarantee long stability of performance and safety features.

The research performed was focused on testing of the stability of surface modification of para-aramid woven fabric using the PACVD technique with the following deposition of fluoropolymer [2]. The idea was to obtain stable modification in the time of storage and usage of the ballistic p-aramid textiles while being resistant against external factors (humidity and/or temperature) with the retention of high performance and safety.

The aim of this study was to evaluate changes in the mechanical and physical properties of PACVD-modified ballistic textiles under the impact of simulated storage conditions in accelerated time using temperature or temperature and humidity as the ageing factors. The accelerated ageing programme was based on [3-5] to allow for assessment of changes in the ageing process of the ballistic materials under various environmental conditions.

Materials

Ballistic woven fabrics

Style 363/120 para-aramid woven fabric (SAATI S.P.A/Italy) was used as a base for the PACVD modification. The main properties of the initial (unmodified) woven fabrics are shown in ***Table 1***.

Ballistic textiles modified by low temperature plasma assisted deposition (PACVD)

The Style 363/120 para-aramid woven fabric was modified by low temperature plasma assisted deposition (PACVD) of fluor-like polymer according to [2] in the PACVD system: CD 400 PLC R/R model (Europlasma/Belgium) using tetradecafluorohexane; (TDFH; Tokyo Chemical Industry/Japan) as a substrate (as a monomer).

Properties of the para-aramid woven fabric modified are listed in ***Table 2***.

Methods

Accelerated ageing of ballistic woven fabrics

The process of accelerated ageing of the unmodified (U/T) and modified (M/T) para-aramid woven fabrics was carried out in an ageing system as described in [6], based on TK 720 apparatus (BINDER GmbH/Germany) for thermal ageing, at 70.0 ± 0.5 °C and as low as possible relative humidity of 15.0 ± 1.5%. Due to the low humidity of the test environment, the temperature was established as the main accelerated ageing agent, as described in [6].

The second accelerated ageing process of unmodified (U/TW) and modified (M/TW) para-aramid woven fabrics 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%.

The periods of ageing were established from experience [3,6] as 28, 35 or 42 days.

Struszczyk MH, Puszkarz AK, Miklas M, Wilbik-Hałgas B, Cichecka M, Urbaniak-Domagała W, Krucinska I. Performance Stability of Ballistic Para-Aramid Woven Fabrics Modified by Plasma-Assisted Chemical Vapour Deposition (PACVD). *FIBRES & TEXTILES in Eastern Europe* 2016; 24, 4(118): 92-97. **DOI:** 10.5604/12303666.1201137

Table 1. Properties of initial unmodified SAATI 363/120 woven fabric (initial ballistic textile).

Surface density, g/m²	Thickness, mm	Breaking strength, N		Elongation at the maximal force, %		Bursting strength, N	Grinding resistance, cycles number	Surface wetting resistance	Water absorption, %	Average water throughput tightness, cm H_2O
PN-ISO 3801:1993	PN-EN ISO 5084:1999	PN-EN ISO 13934-1:2002				PN-EN 863:1999	PN-EN ISO 12947-1:2000+AC:2006 PN-EN ISO 5470-2:2005	PN-EN 24920:1997	PN-EN 29865:1997	
		lengthwise	crosswise	length-wise	cross-wise					
212 ± 3	0.20 ± 0.02	6700 ± 200	6800 ± 200	7.0	5.1	79.0 ± 10.0	16 000	1; 1; 1	30.4 ± 0.5	23.0

Table 2. Properties of initial SAATI 363/120 woven fabric modified by the low temperature plasma deposition of fluoropolymer.

Surface density, g/m²	Thickness, mm	Breaking strength, N		Elongation at the maximal force, %		Bursting strength, N	Grinding resistance, cycles number	Surface wetting resistance	Water absorption, %	Average water throughput tightness, cm H_2O
PN-ISO 3801:1993	PN-EN ISO 5084:1999	PN-EN ISO 13934-1:2002				PN-EN 863:1999	PN-EN ISO 12947-1:2000+AC:2006 PN-EN ISO 5470-2:2005	PN-EN 24920:1997	PN-EN 29865:1997	
		lengthwise	crosswise	length-wise	cross-wise					
210 ± 3	0.20 ± 0.02	7800 ± 176	9500 ± 499	7.3	5.2	65.0 ± 24.0	45 000	4; 4; 3	30.3 ± 1.7	1.0

Properties of the unmodified and modified ballistic woven fabrics

The range of properties of the unmodified and modified ballistic woven fabrics before and after accelerated ageing was established as a result of elaborated risk analysis specifying the main hazardous events with the relation to the behaviour of the fabrics as well as to their performance and safety.

The properties of ballistic woven fabrics were determined as described in ***Tables 1** & **2***, i.e.: surface density according to PN-ISO 3801-1993, thickness according to PN-EN ISO 5084:1999, tear resistance according to PN-EN ISO 13937-2:2002, breaking strength and elongation at the maximal force according to PN-EN ISO 13934:2002, bursting strength according to PN-EN 863:1999, surface wetting resistance according to PN-EN 24920:1997, water absorption and the average water throughput tightness resistance according to PN-EN 29865:1997. The apparent density was calculated as a division of the surface density by the thickness.

The abrasion resistance was estimated on the basis of Standards PN-EN ISO 12947-1:2000+AC:2006 and PN-EN ISO 5470-2:2005. During the test, the number of grinding cycles till destruction of the sample was determined.

Results and discussion

The change in thickness and surface density of the para-aramid woven fabrics modified by PACVD or unmodified during the accelerated ageing process using the temperature or temperature and relative high humidity is presented in ***Figures 1** & **2***.

The process of accelerated ageing caused an insignificant reduction in the unmodified woven fabrics when the temperature was used as the accelerated ageing factor. A similar phenomenon was detected when estimating the surface density: a reduction in this parameter for the unmodified woven fabrics showed a higher tendency as compared with the PACVD-modified textile. The above observations lead to the conclusion that the process of accelerated ageing resulted in a looser structure of the unmodified woven. For visualisation of the above phenomenon, the apparent density of the textiles tested was calculated. The values of apparent density of the unmodified textiles changed from an initial value of 603.1 kg/m³ to 632.5 kg/m³ after 42 days of accelerated ageing, resulting from the consolidation of the spatial structure. A similar observation was made with the modified textiles, where an increase from 646.2 to 659.4 kg/m³ was detected.

When the temperature and humidity were applied as the ageing factors, an insignificant reduction in the thickness of the woven fabric was observed for both

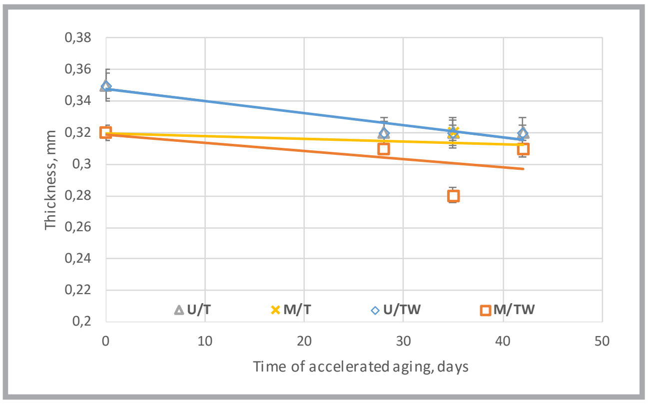

Figure 1. Effect of accelerated aging at a temperature of 70 °C (U/T; M/T) or temperature of 70 °C and relative humidity of 65% (U/TW; M/TW) on the thickness of the modified and unmodified para-aramid woven fabrics.

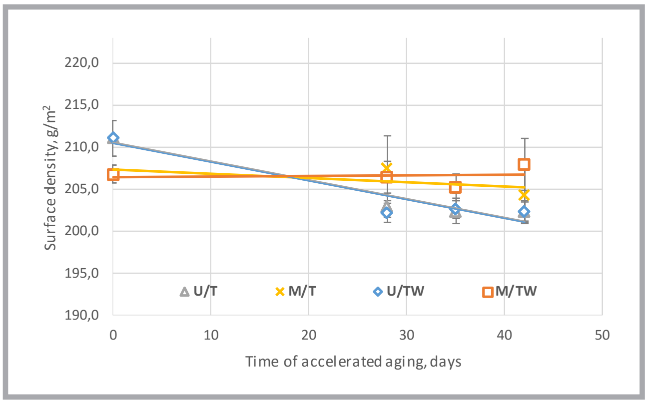

Figure 2. Effect of accelerated aging at a temperature of 70 °C (U/T; M/T) or temperature of 70 °C and relative humidity of 65% (U/TW; M/TW) on the surface density of the modified and unmodified para-aramid woven fabrics.

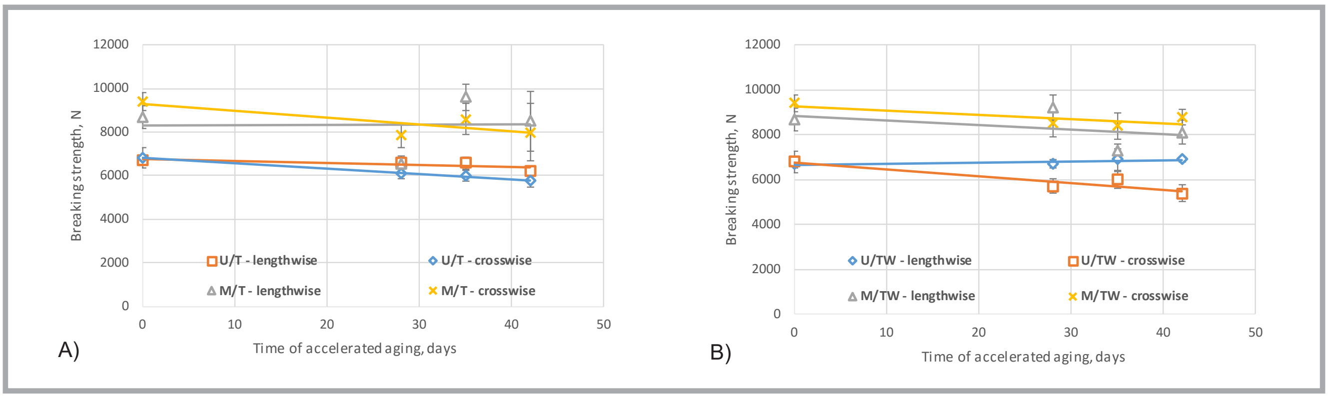

***Figure 3.** Effect of accelerated aging at a temperature of 70 °C (A: U/T; M/T) or temperature of 70 °C and relative humidity of 65% (B: U/TW; M/TW) on the breaking strength of the modified and unmodified para-aramid woven fabrics.*

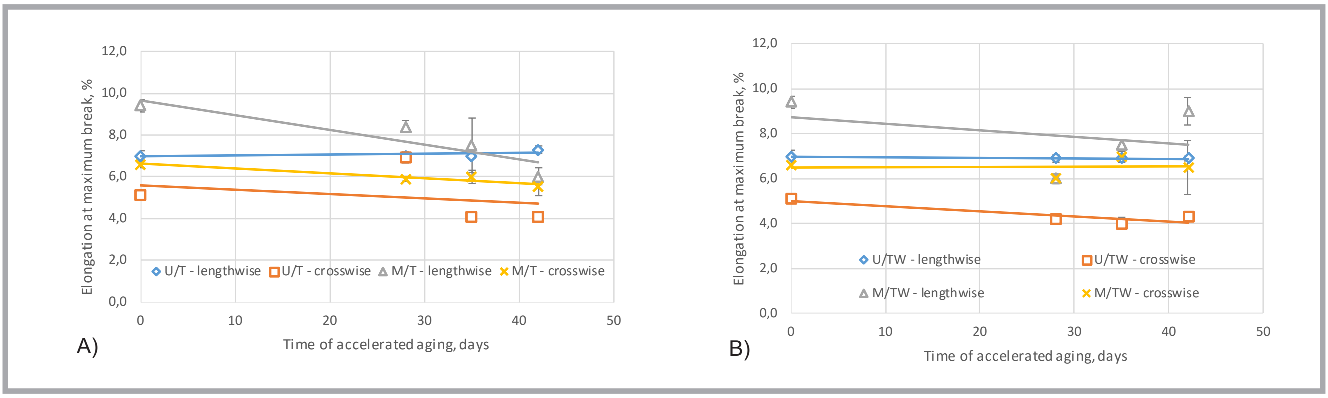

***Figure 4.** Effect of accelerated aging at a temperature of 70 °C (A: U/T; M/T) or temperature of 70 °C and relative humidity of 65% (B: U/TW; M/TW) on the elongation of the modified and unmodified para-aramid woven fabrics.*

of the PACVD-modified and unmodified materials. A lower tendency of changes was found in the PACVD-modified textiles. Stability of the areal density of the PACVD modified samples was observed. This parameter of the unmodified woven material decreased during accelerated ageing by approx.10% as compared with the initial value, with a similar tendency observed when only the temperature was used as the accelerated ageing factor. The apparent density of the unmodified woven fabrics changed from 603.1 kg/m^3 to a minimal value of 631.9 kg/m^3 after 25 days of ageing, resulting in consolidation of the textile structure. A similar phenomenon was found in the PACVD-modified textiles, where the apparent density increased from the initial value of 646.2 kg/m^3 to a maximal value of 732.8 kg/m^3 after 35 days of ageing, with a reduction to 671.0 kg/m^3 after 42 days of ageing.

The effects of accelerated ageing on the maximal breaking strength and elongation at break of the unmodified and PACVD-modified woven fabrics are shown in ***Figures 3** & **4***.

Similar changes in the breaking strength of unmodified and PACVD-modified para-aramid fabrics were observed. The initial PACVD-modified woven fabric showed a higher value of the parameter mentioned, measured both lengthwise and crosswise.

Moreover the elongation parameter of the unmodified textile determined in the lengthwise direction did not show significant change in the process of accelerated ageing when the temperature was used as the ageing factor. When the elongation was measured in the crosswise direction, a reduction in the parameter was observed, both for unmodified and PACVD-modified samples (by approx. 0.5% - 2.5%).

The application of temperature and humidity during the accelerated ageing yielded a similar change in behaviour of unmodified and PACVD-modified samples when the breaking strength was measured in the lengthwise direction. The initial, unmodified textiles showed higher values of breaking strength, both crosswise and lengthwise. In the case of the breaking strength determined in the crosswise direction, the parameter was found to be stable during the accelerated ageing process of the unmodified textiles.

The elongation at the maximal force in the crosswise direction in the unmodified material or for the lengthwise direction in the PACVD-modified textiles did not show any significant changes during the accelerated ageing process. In other cases, an insignificant decrease in elongation at the maximal force was observed.

The tear resistance of unmodified and PACVD-modified fabrics after accelerated ageing with temperature or temperature and humidity is presented in ***Tables 3** & **4***.

The process of the accelerated ageing with the temperature after 28 days caused the destruction of the woven textiles, both unmodified and PACVD-modified, with the continuity of fibres remaining, identical to that observed for the initial materials. After 35 days of ageing, the absence of tearing and loosening effects of the textile structure was observed in the modified samples.

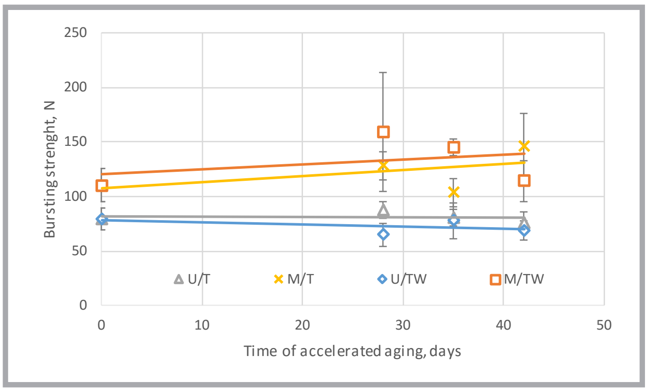

Figure 5. *Effect of accelerated aging at a temperature of 70 °C (U/T; M/T) or temperature of 70 °C and relative humidity of 65% (U/TW; M/TW) on the bursting strength of the modified and unmodified para-aramid woven fabrics.*

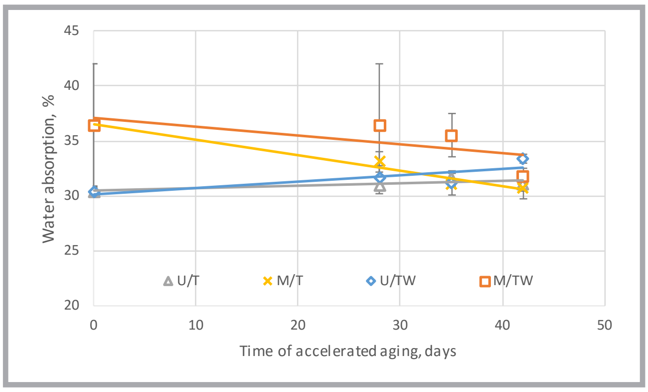

Figure 6. *Effect of accelerated aging at a temperature of 70 °C (U/T; M/T) or temperature of 70 °C and relative humidity of 65% (U/TW; M/TW) on the water absorption of the modified and unmodified para-aramid woven fabrics.*

The above phenomenon is probably synergistically connected with the low temperature plasma treatment as well as with an increase in temperature during the accelerated ageing. It can be attributed to the creation of physical and/or chemical interactions induced on a microscale by the increase in adhesion between single fibres, assuming the consolidation of the woven structure.

If the temperature and humidity were used as the ageing factors, the destruction of the woven structure was observed in the unmodified samples, similar to the effect detected in the initial ones. In the PACVD-modified samples, the effect above was not found under test conditions. The PACVD-modified textiles maintained their integration, which was identical to the ageing using temperature only; however, the effect appeared more quickly and only in the PACVD modified samples.

The effect of accelerated ageing on the bursting strength of the unmodified and PACVD modified textiles is shown in ***Figure 5***.

The process of accelerated ageing conducted with temperature did not affect the bursting strength of the unmodified textiles, whereas the prolongation of ageing yielded an increase in this parameter in the PACVD-modified samples. The effect observed is related to the tearing resistance observation. An increase in interfilament adhesion resulted in structure consolidation, and finally induced an increase in the bursting resistance.

When the temperature and humidity were used as the ageing factors, the process of accelerated ageing did not affect the bursting strength of the unmodified samples. The PACVD modification yielded a significant increase in the bursting strength with the prolongation of accelerated ageing. The effect observed was higher (by approx. 20% after 28 days and 30% after 35 days), as compared with the accelerated ageing process, where only temperature was used as the testing factor.

Figure 6 shows the relationship between water absorption and the conditions as well as the time of accelerated ageing of the unmodified or PACVD-modified para-aramid woven fabrics.

The process of accelerated aging with temperature or temperature and humidity as the ageing factor caused a decrease in water absorption in the PACVD-modified samples. After 35 days (ageing factor: temperature) or 45 days (ageing factor: temperature and humidity) of ageing the modified textile, the water absorption reached a value similar to that of the unmodified material.

The application of temperature and humidity during the accelerated ageing yielded a insignificant increase in that parameter during the test.

The effect of accelerated ageing on the average water throughput tightness

Table 3. *Tear resistance in N of unmodified and PACVD-modified fabrics after accelerated ageing with temperature. [1)] – effect detected was the result of looser yarns instead of torn ones.*

Direction of tearing	Accelerated ageing period, days							
	U	M	U/T			M/T		
	0		28	35	42	28	35	42
Lengthwise	673 ± 70[1)]	434 ± 90[1)]	670 ± 133[1)]	688 ± 274[1)]	735 ± 73[1)]	501 ± 55[1)]	No tearing	No tearing
Crosswise	695 ± 72[1)]	556 ± 104[1)]	738 ± 60[1)]	664 ± 127[1)]	619 ± 62[1)]	662 ± 129[1)]		

Table 4. *Tear resistance in N of unmodified and PACVD-modified fabrics after accelerated ageing with temperature and humidity, [1)] – effect detected was the result of looser yarns instead of torn ones.*

Direction of tearing	Accelerated ageing period [days]							
	U	M	U/TW			M/TW		
	0		28	35	42	28	35	42
Lengthwise	673 ± 70[1)]	434 ± 90[1)]	657 ± 92[1)]	605 ± 70[1)]	650 ± 72[1)]	No tearing	No tearing	No tearing
Crosswise	695 ± 72[1)]	556 ± 104[1)]	700 ± 143[1)]	695 ± 90[1)]	643 ± 143[1)]			

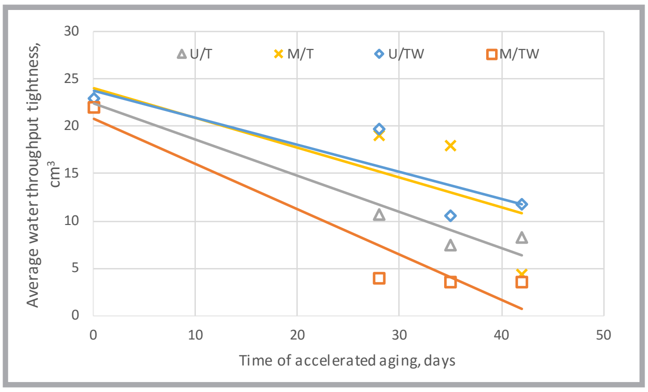

***Figure 7.** Effect of accelerated aging at a temperature of 70 °C or temperature of 70 °C and relative humidity of 65% on the average water throughput tightness of the modified and unmodified UHMWPE fibre composites.*

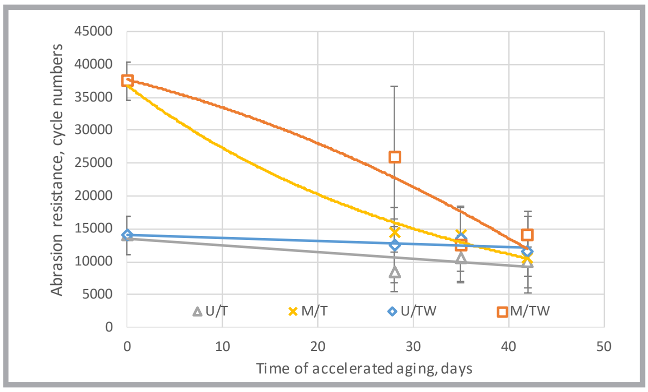

***Figure 8.** Effect of accelerated aging at a temperature of 70 °C or temperature of 70 °C and relative humidity of 65% on the abrasion resistance of the modified and unmodified UHMWPE fibre composites.*

of the unmodified and PACVD-modified textiles is shown in ***Figure 7***.

Prolongation of the accelerated process resulted in a decrease in the average water throughput tightness of the unmodified and PACVD-modified textiles when the temperature or temperature and humidity were used as the ageing factors. After 28 days of the research with temperature and humidity, this parameter of the PACVD-modified samples was found to have reduced by approx. 80% as compared with the initial value. The reduction was lower (by approx. 15%) compared to the unmodified fabric or PACVD-modified samples aged using temperature only.

The process ran more dynamically but insignificantly in the woven material modified by PACVD.

If the process of ageing was combined with temperature and humidity, a similar observation was made.

Semi-quantitative results of changes in the average surface wetting resistance for unmodified and PACVD modified textiles after accelerated ageing are shown in ***Tables 5** & **6***.

The accelerated ageing process with temperature caused a reduction in the surface wetting resistance of the PACVD-modified textiles after the first period of ageing from 3 (wetting at the point of water dropping) to 2 (wetting of 50% of the surface tested). Then the parameter was stable during the whole period of accelerated ageing. Full surface wetting was observed for the unmodified samples initially and during the process of ageing. When the humidity and temperature were applied as the ageing factors, an increase in the surface wetting resistance of the PACVD-modified material from 3 (wetting at the point of water dropping) up to 4-5 (limited or absence of wetting) was detected after 35 days of ageing. Prolongation of the test did not induce any changes in the surface wetting resistance. The unmodified sample showed stable surface wetting resistance amounting to 1 during the accelerated ageing.

***Table 5.** Semiquantitative results of changes in the average surface wetting resistance for unmodified and PACVD-modified textiles after accelerated ageing with temperature.*

Parametr	Accelerated ageing period [days]							
	U	M	U/TW			M/TW		
	0		28	35	42	28	35	42
Average surface wetting resistance	1	3	1	1	1	2	2	2

***Table 6.** Semiquantitative results of changes in the average surface wetting resistance for unmodified and PACVD modified textiles after accelerated ageing with temperature and humidity.*

Parametr	Accelerated ageing period [days]							
	U	M	U/TW			M/TW		
	0		28	35	42	28	35	42
Average surface wetting resistance	1	3	1	1	1	3	4 - 5	4 - 5

The effect of accelerated ageing on the abrasion resistance of the unmodified and PACVD modified woven fabrics is shown in ***Figure 8***.

PACVD modification of the para-aramid woven fabrics improved the resistance against abrasion, defined as the maximal number of cycles, which did not cause the destruction of the sample tested. Based on the test results of the initial materials, it can be concluded that the process of PACVD modification provided a more than 2.5-fold increase in the abrasion resistance of para-aramid fabrics. During the accelerated ageing with a temperature of 70 °C, the abrasion resistance of PACVD-modified textiles decreased, but the reduction rate was significantly lower as compared with unmodified samples: by approx. 70% after 28 days, approx. 30% after 35 days and approx. 5% after 42 days of ageing.

The process of accelerated ageing where temperature and humidity was used, lowered the abrasion resistance of the PACVD modified textiles, but higher values were found as compared with unmodified materials: by approx. 110% after 28 days, approx. 20% after 42 days of ageing.

No statistical change in the abrasion resistance of the unmodified samples was found during the accelerated ageing using both sets of conditions.

Conclusions

The modification of p-aramid textile using PACVD followed by deposition of fluoropolymer yielded significant changes in the properties of the materials tested. A superhydrophobic surface of fibres is formed, which affects the resistance against destructive, external factors. Mechanical properties of the PACVD-modified ballistic textiles showed prolonged stability of the performance and safety features during the simulated accelerated aging test when the temperature as well as temperature and relatively high humidity were applied.

Based on the results obtained, it can be concluded that PACVD followed by deposition of fluoropolymer onto the surface of p-aramid ballistic textiles is a promising, economical and environmental-friendly technique that allows to prolong the usage of ballistic protectors.

Verification of the ballistic properties of un- and PACVD-modified p-aramid woven fabrics according to the PN-V-87000 Standard for the initial materials as well as after accelerated aging will be the next stage of the research. Additionally the effect of potential changes in the structural properties after the accelerated aging test will also be studied.

Acknowledgements

The research was supported by the National Science Centre under research project No. N N508 629940 „THE STUDIES ON THE FUNCTIONALISATION OF BALLISTIC MATERIALS”.[1]

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Received 19.08.2015 Reviewed 15.02.2016