Marcin Łandwijt[1,*],
Marcin H. Struszczyk[1],
Wiesława Urbaniak-Domagała[2],
Adam K. Puszkarz[2],
Bożena Wilbik-Hałgas[1],
Magdalena Cichecka[1],
Izabella Krucińska[2]

Ballistic Behaviour of PACVD-Modified Textiles

DOI: 10.5604/01.3001.0012.7512

[1] **Institute of Security Technologies "MORATEX",**
ul. Sklodowskiej-Curie 3, 90-505 Lodz, Poland
* e-mail: mlandwijt@moratex.eu

[2] **Lodz University of Technology, Faculty of Material Technologies and Textile Design, Department of Material and Commodity Sciences and Textile Metrology,**
ul. Zeromskiego 116, 90-924 Lodz, Poland

Abstract
A comprehensive study was performed using the Plasma Assisted Chemical Vapour Deposition (PACVD) modification of ultrahigh molecular weight polyethylene (UHMWPE) fibrous composites and paramid fabrics with the deposition of fluoro-or silane-like-polymer onto their surface. Research on the resistance to fragments was performed on the basis of our own testing procedure elaborated on the basis of the STANAG 2920 Ballistic Test Method For Personal Armour Materials And Combat Clothing, revision 2. The model insert systems made of the modified or unmodified unwoven sheets of UHMWPE fibres exhibited significantly different trends of changes in fragment-proofness when the temperature together with humidity were applied as the ageing factors. In the inserts made of modified unwoven sheets, an increase in the V50 value was observed, while the V50 of the inserts made of unmodified sheets decreased along with the extension of the accelerated ageing process. Modification with low-temperature plasma in the presence of vapours of low-molecular fluorine- or silane-genic substrates altered the properties of the fabrics and unwoven sheets. PACVD modification allows to prevent the destructive influence of humidity during the aging process.

Key words: *PACVD-modified textiles, ballistic compositions, accelerated ageing.*

Introduction

The stability of the ballistic protection's performance during use and storage is a main factor affecting its safety. The application of a physical barrier (semi-permeable textile covers) of ballistic inserts allows to partially limit the risk of degradation of the ballistic materials accelerated by humidity (external – rain; internal – sweet) and/or temperature [1,2]. The possibility of the direct prevention of ballistic textiles and fibrous-originated composites, allowing prolongation of the safe use of ballistic protectors and to reduce the cost of manufacture with limitation of environmentally unfriendly wastes was the main aspects of [3,4].

The effect of accelerated ageing on the main physico-mechanical and structural properties was tested using PACVD-modified soft UHMWPE fibrous composites and p-aramid woven fabric with the deposition of silane-like- or fluoropolymer onto surfaces. The accelerated ageing of PACVD-modified textiles confirmed the significant effect of the surface-deposited polymer on the main performance of the ballistic textile and a protection effect against the ageing factors, varying in relation to the type of accelerated ageing factor used.

Moreover the accelerated ageing of PACVD-modified p-aramid fabrics by the deposition of fluoropolymer indicated the initiation of superhydrophobic behaviour, significantly supporting resistance against the degradation following lost mechanical strength [5].

PACVD modification of a textile surface should not affect the ballistic resistance and ought to prevent the stability of the above-mentioned functionality during long-term use and storage. Taking into account the above, the aim of the study was to evaluate:
1) the effect of PACVD modification of both types of ballistic textiles: p-aramid woven fabric and UHMWPE fibrous composites on the ballistic behaviour shown by the bullet- and fragment proofness, and
2) the stability of the ballistic behaviour of the PACVD-modified materials during simulated ageing using temperature or temperature and humidity.

Materials

Textile materials

Two types of the ballistic textiles were used in the research:
- Woven fabric Style 363/120 (SAATI S.P.A, Italy), made of p-aramid yarns;
- Dyneema® SB51 UHMWPE fibrous composite (DSM/The Netherlands) [6].

In order to perform tests of ballistic properties and accelerated ageing during the optimisation research, ballistic insert model systems were designed, which constituted ballistic packets consisting of:
- 38 layers of p-aramid woven fabric Style 363/120 (PACVD-modified or unmodified)
- 22 unwoven sheets of UHMWPE fibres (PACVD-modified or unmodified).

After the process of accelerated ageing, the insert model systems underwent further research for verification of the result stability of the process of modification with lowtemperature plasma in the presence of vapours of tetradecafluorohexane (TDFH) or hexamethyldisiloxane (HMDSO) regarding their ballistic properties.

Substrates for PACVD (Plasma Assisted Chemical Vapour Deposition)

Dyneema SB51 was PACVD-modified using hexamethyldisiloxane ($C_6H_{18}OSi_2$; HMDSO) from Sigma Aldrich, whereas for surface PACVD modification of p-aramid woven fabric, tetradecafluorohexane; $CF_3(CF_2)_4CF_3$; (TDFH), 99%, from Tokyo Chemical Industry/Japan was used.

Methods

Surface modification of Dyneema® SB51 by PACVD

The modification of Dyneema® SB51 in glow discharges was performed in a commercial plasma jet – CD 400PLC ROLL CASSETTE (EUROPLASMA/ Belgium) according to [7] using the following process parameters:
- for PACVD-modified Dyneema® SB51: polymerisation in a stream of HMDSO at a flow rate of 0.032 Pa $m^3 s^{-1}$ with a power of 100 W applied to the electrodes, for a time of 3 min.

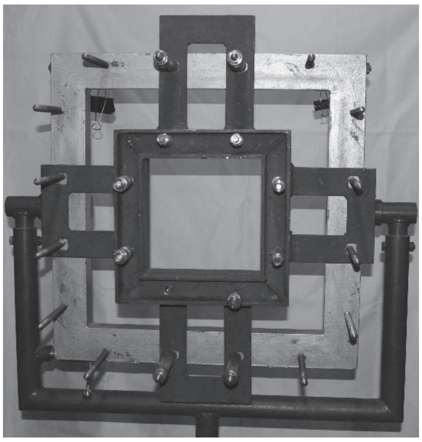

Figure 1. Test stand for fixing unconventional, small-sized test samples (250 x 250 mm).

- for PACVD modified p-aramid Style 363/120 woven fabric: polymerisation in astream of tetradecafluorohexane at a flow rate of: 0.032-0.064 Pa m^3 s^{-1}, with a power of 200 W applied to the electrodes, for a time period of 1 min.

Accelerated ageing
The process of accelerated ageing of the ballistic insert model system (modified and unmodified variants) was carried out according to [7].

Research on the resistance to fragments
Research on the resistance to fragments was performed on the basis of our own testing procedure – PBB-26 "Ballistic tests. Determining the fragment-proofness of a set of samples" elaborated on the basis of the STANAG 2920 Ballistic Test Method For Personal Armour Materials And Combat Clothing, revision 2.

Research on the ballistic limit velocity V50 with use of a 1.10 ± 0.03 g standard fragment of FSP 22 was performed for samples of 250 x 250 mm size, subjected to thermo-stating at 20 ± 3 °C and relative humidity of 65 ± 5% for a time period not shorter than 5 hours. Furthermore the packet was fixed on a test stand of dedicated design that allowed for testing samples of small dimensions (***Figure 1***).

The model insert systems were shot at least 4 times in a manner so that the hit spots appear at least 30 mm from the sample edge, fixing elements and previous hit points. The ballistic limit velocity V50 (the velocity of a fragment at which the probability of piercing a material being tested reaches 50%) was calculated, as the mean of the three highest hit velocities resulting in partial penetration and the three lowest hit velocities resulting in full piercing, provided that no difference between the velocities exceeded 40 m/s. In cases where the value of velocity difference exceeded 40 m/s, the testing was continued until a difference no bigger than 50 m/s was achieved between the five highest and five lowest velocities.

Research on the resistance to bullets
The resistance to bullets was tested on the basis of the PN-V-87000:2011 Standard, with the use of a 7,62 x 25 TT bullet with a lead core and bi-metallic jacket of a mass of 5.5 ± 0.1g, at a velocity of 420 ± 15 m/s (class K2).

The research was performed on samples of 250 x 250 mm, subjected to thermo-stating at a temperature of 20 ± 3 °C and relative humidity of air of 65 ± 5% for a time period no shorter than 5 hours. Moreover the research included assessment of the number of penetrated layers of the insert model system as well as of the depth of the momentary, dynamic deflection of an insert by measuring the depth of deformation of the ballistic base behind the insert.

Results and discussion

Research on the resistance to fragments

Every test was performed on 2 insert model systems, with the calculation of V50 and Δ for each sample, and consequent calculation of the mean of aggregate results of 2 insert model systems.

The periods of accelerated ageing were chosen based on the experiments of previously completed research projects involving the accelerated ageing of ballistic materials, which concluded that the period between 28 and 42 days, which corresponds to 3 years of ageing of ballistic materials under real conditions, is critical concerning the changes in their properties.

Research on the resistance to bullets
Figure 2 presents the dependence of the V50 of the ballistic model systems made of modified and unmodified woven fabrics on the time of the accelerated ageing process where the ageing factor was the temperature only.

It was found that the greatest changes in V50 occurred after the first 28 days of accelerated ageing of the ballistic model systems, which corresponds to 2 years of ageing under real conditions. The trend of changes was similar for both ballistic model systems of modified and unmodified fabrics

The ***Figure 3*** presents the dependence of V50 assessed for the ballistic model systems made of modified (A/M) and unmodified (A/N) p-aramid woven fabrics on the time of the accelerated ageing process where the ageing factor was the temperature together with humidity.

The introduction of an additional ageing factor – humidity, made the changes observed more dynamic with a similar trend to that of the inserts aged with the temperature factor only. The largest decrease in V50 occurred in the inserts made of unmodified fabrics (ca. 11% compared to the initial value after 42 days of accelerated ageing). In the inserts with modified fabric, the decrease was lower by half (ca. 5% compared to the initial value).

Model insert systems made of modified or unmodified unwoven sheets of UHMWPE fibres
Figure 4 presents the dependence of the V50 of the model insert systems made of modified and unmodified unwoven sheets on the time of accelerated ageing where the only ageing factor was the temperature.

A similar trend of V50 changes to that of the model insert systems made of p-aramid fabrics was observed in the inserts of modified and unmodified unwoven sheets, provided they were aged with the temperature agent. No remarkable differences in V50 were observed in dependence on neither the time of accelerated ageing, nor on the modifications of the sheet's surface.

Figure 5 presents the dependence of the V50 of the model insert systems made of modified and unmodified unwoven sheets on the time of the accelerated ageing process where the temperature with humidity were the ageing factors.

In the process of ageing where the temperature together with humidity were the ageing factors, a remarkable reduction in V50 was observed in the course of the accelerated ageing of the model insert systems comprising unmodified unwoven sheets. In the case of the model in-

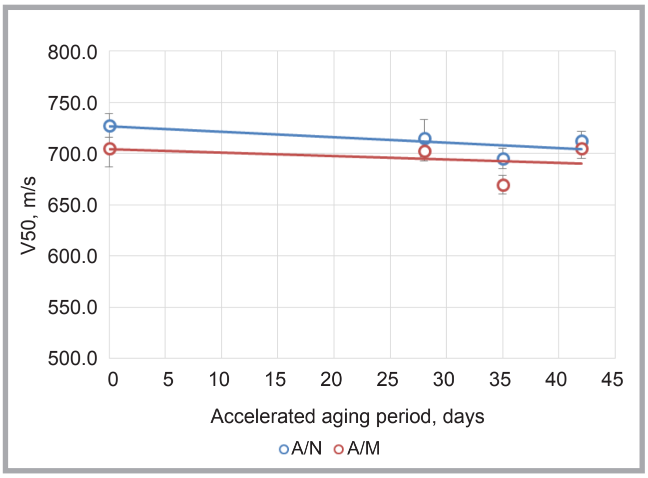

***Figure 2.** Dependence of V50 assessed for the ballistic model systems made of modified (A/M) and unmodified (A/N) p-aramid woven fabrics on the time of the accelerated ageing process where the ageing factor was the temperature only.*

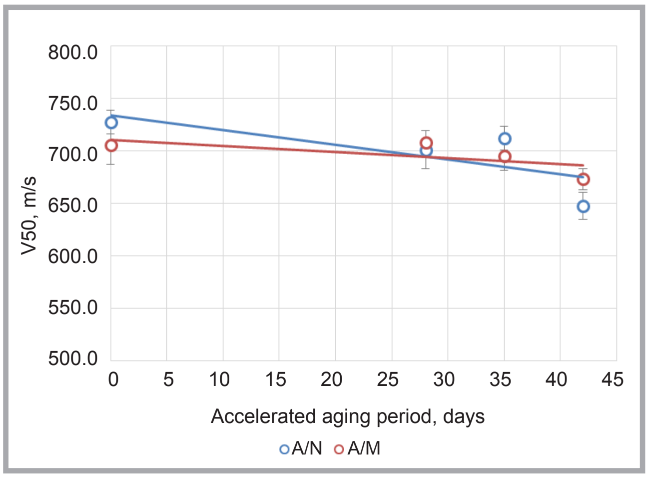

***Figure 3.** Dependence of V50 assessed for the ballistic model systems made of modified (A/M) and unmodified (A/N) p-aramid woven fabrics on the time of the accelerated ageing process where the ageing factor was the temperature together with humidity.*

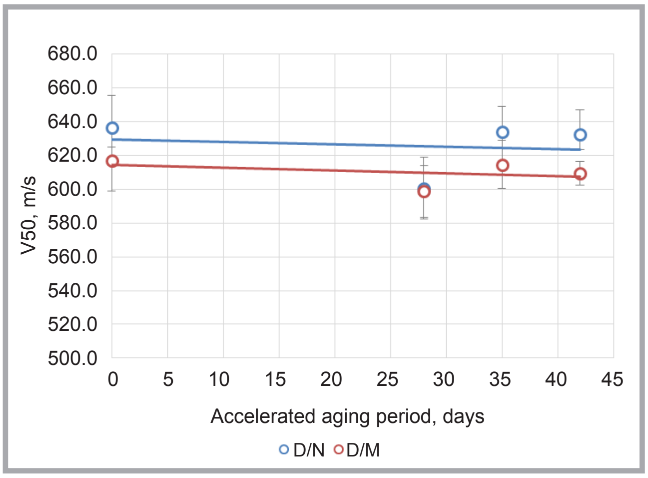

***Figure 4.** Dependence of V50 assessed for the ballistic model systems made of modified (D/M) and unmodified (D/N) unwoven sheets on the time of accelerated ageing where the only ageing factor was the temperature.*

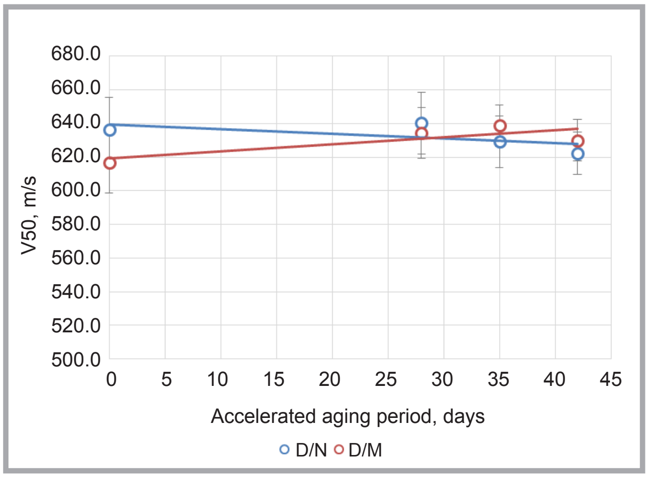

***Figure 5.** Dependence of V50 assessed for the model insert systems made of modified (D/M) and unmodified (D/N) unwoven sheets on the time of the accelerated ageing process where the temperature with humidity were the ageing factors.*

sert systems made of modified unwoven sheets, a remarkable increase in V50 was observed in the course of the accelerated ageing process, though the interpretation of the phenomenon above is difficult.

Research on bullet-proofness

According to the requirements of the K2 class of the model insert systems, tests of bullet-proofness were performed on the inserts before and after successive periods of accelerated ageing.

No case of full piercing occurred in the model insert systems made of textile materials subjected to modification with low-temperature plasma in the presence of TDFH or HMDSO vapours.

In the unmodified samples, either based on the p-aramid fabrics or unwoven sheets of UHMWPE fibres, full piercing with the bullet was observed in the samples after accelerated ageing, consecutively in the model insert system based on the unmodified Style 363/12 fabrics and on the unwoven sheets – after 42 days of ageing where the temperature was the only ageing factor.

The research included assessing two additional parameters: the number of the model insert system layers penetrated with the bullet and the depth of the temporary, dynamic deflection of the insert by measuring the depth of deformation of the ballistic base behind the system tested. In the case of full piercing of the model system, the total number of layers was recorded as the number of penetrated layers, and the maximum permissible value of 40 mm was recorded as the observed deflection.

Model insert systems of unmodified or modified p-aramid fabrics

The dependence of the mean value of the number of layers penetrated by a bullet in the model insert systems of modified and unmodified p-aramid fabrics assessed, on the time of the accelerated ageing process where temperature was the only ageing factor is presented in ***Figure 6***.

In the inserts developed with the modified systems, a decrease was observed in the mean value of the number of fabric layers penetrated by the bullet, unlike the insert systems made of unmodified fabrics. However, the changes above were insignificant in the light of statistical analysis.

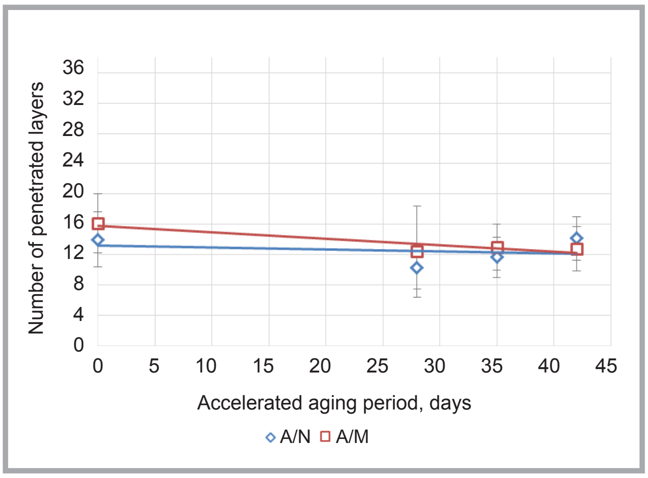

Figure 6. *Dependence of the mean value of the number of layers penetrated by a bullet in the model insert systems of modified (A/M) and unmodified (A/N) p-aramid fabrics assessed, on the time of the accelerated ageing process where the temperature was the only ageing factor.*

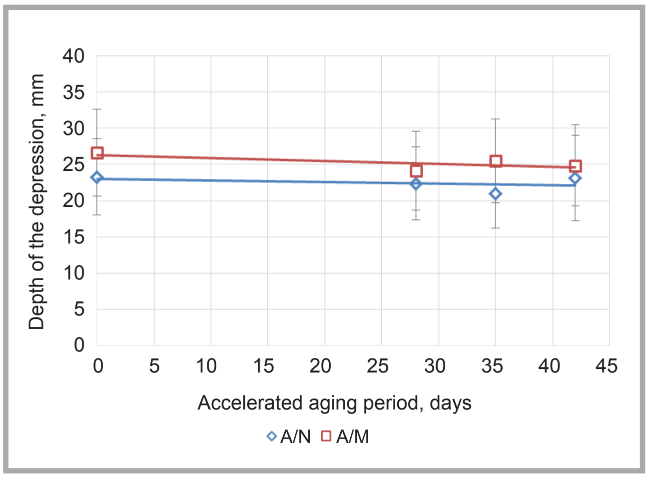

Figure 7. *Dependence of the ballistic base deformation depth for the model insert systems of the modified (A/M) and unmodified (A/N) p-aramid fabrics assessed on the time of the accelerated ageing process where the temperature was the only ageing factor.*

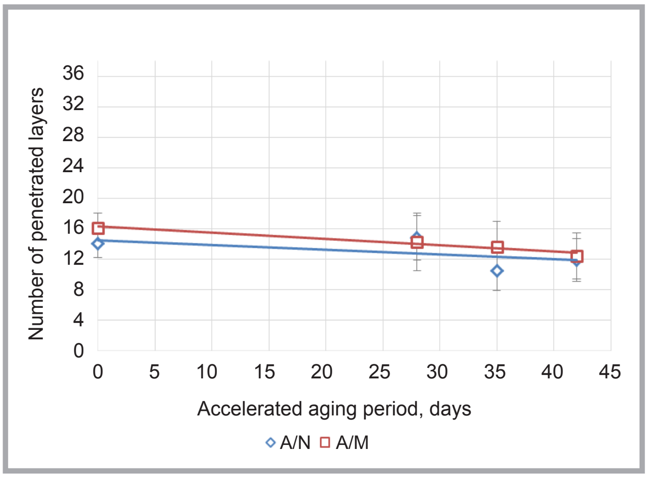

Figure 8. *Dependence of the mean number of layers penetrated by a bullet for the model insert systems of modified (A/M) and unmodified (A/N) p-aramid fabrics assessed on the time of the accelerated ageing process where the temperature with humidity were the ageing factors*

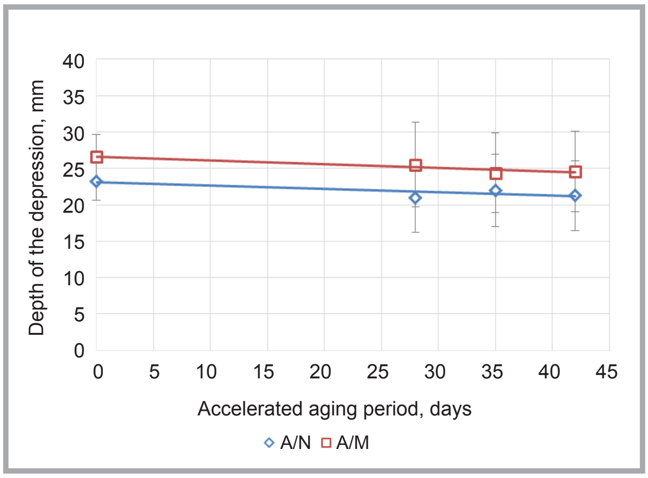

Figure 9. *Dependence of the base deformation on the time of the accelerated ageing process in the model insert systems of modified (A/M) and unmodified (A/N) p-aramid fabrics assessed where the temperature with humidity were the ageing factors*

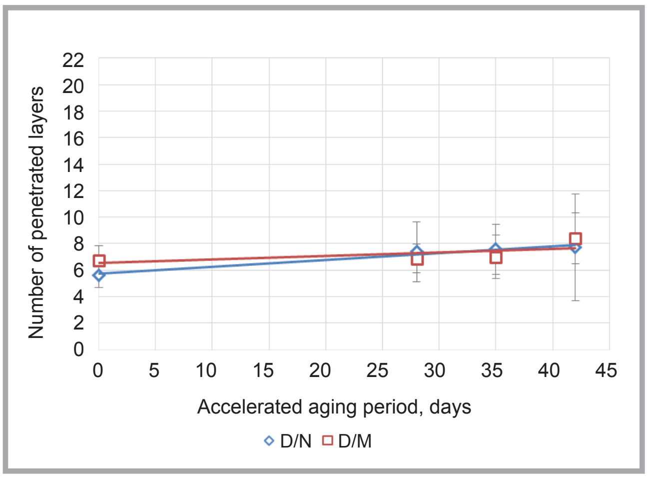

Figure 10. *Dependence of mean number of the layers penetrated with a bullet in assessed model insert systems with the modified (D/M) an modified (D/N) unwoven sheets on the time of accelerated ageing process where the temperature was the only ageing factor*

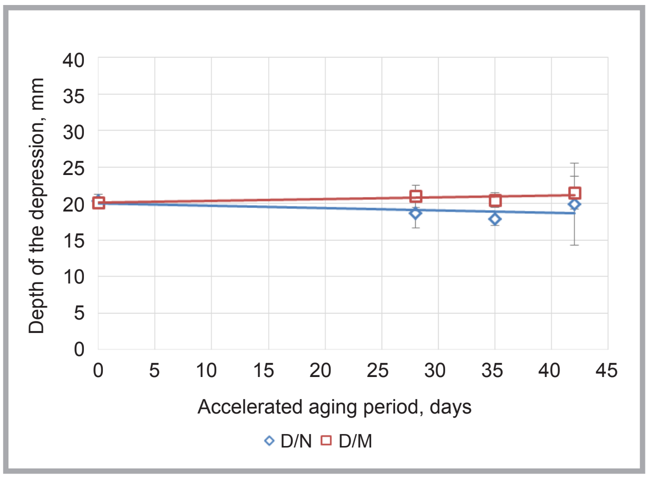

Figure 11. *Dependence of the mean value of base deformation in the model insert systems made of modified (D/M) and unmodified (D/N) unwoven sheets assessed on the time of the accelerated ageing process where the temperature was the only ageing factor*

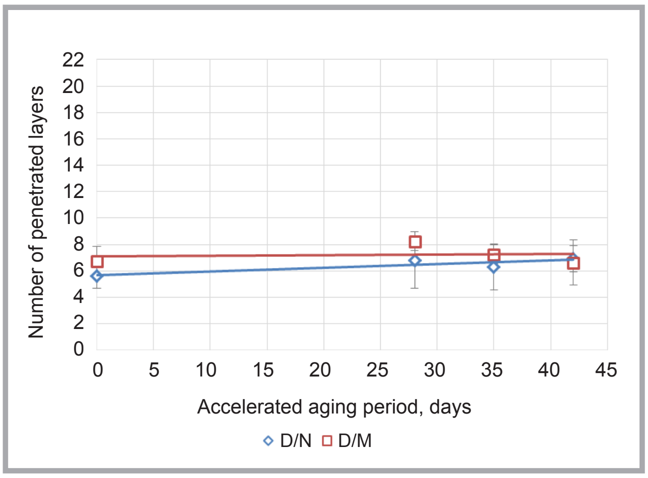

***Figure 12.** Dependence of the mean number of layers penetrated by the bullet in the model insert systems made of the modified (D/M) an unmodified (D/N) unwoven sheets assessed on the time of the accelerated ageing process where the temperature with humidity were the ageing factors.*

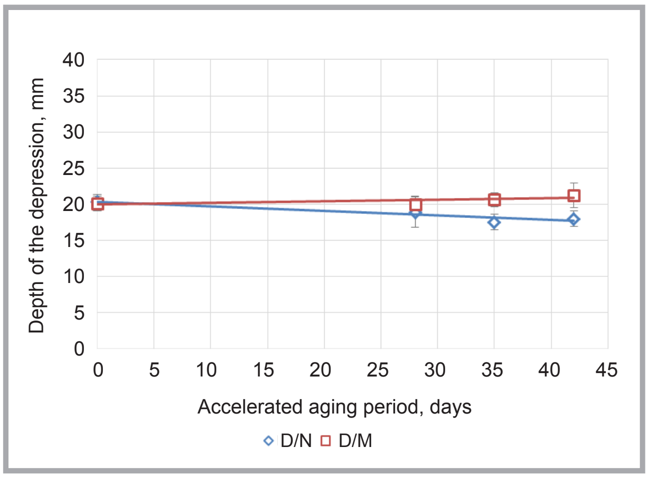

***Figure 13.** Dependence of base deformation in the model insert systems made of modified (D/M) and unmodified (D/N) unwoven sheets assessed on the time of the accelerated ageing process where the temperature with humidity were the ageing factors.*

Figure 7 presents the dependence of ballistic base deformation for the insert model systems of modified and unmodified p-aramid fabrics assessed on the time of the accelerated ageing process where the temperature was the only ageing factor.

The model insert systems made of fabrics subjected to modification were characterised with a slightly bigger mean deflection of the ballistic base compared to the unmodified systems, which may be linked to the decrease in the multidirectional strength (perforation) of the single layers observed during the mechanical tests (this might be due to loosening of the fabric structure in the modification process during preparation of samples for processing). Along with prolongation of the accelerated aging process, the average depth of the deformation decreased, at a lower rate in the systems with modified fabrics.

In the case of prolongation of the accelerated ageing process where the temperature together with humidity were the ageing factors, a decrease was observed in the mean number of penetrated layers in the model insert systems, both in samples made of unmodified fabrics and in the modified ones (***Figure 8***). The differences between the mean numbers of layers penetrated in the inserts made of the modified and unmodified fabrics were statistically insignificant.

Figure 9 presents the dependence of the base deflection for the model insert systems of modified and unmodified p-aramid fabrics assessed on the time of the accelerated ageing process where the temperature together with humidity were the ageing factors.

A trend similar to that observed when the ageing factor was the temperature alone (decrease in the average deformation depth of the base during aging) was observed in accelerated ageing with the temperature and humidity together.

As in ageing with the temperature factor, mean values of the depth of base deformation were lower in the model insert systems made of unmodified p-aramid fabrics.

Model insert systems of unmodified or modified unwoven sheets of UHMWPE fibres

For the model insert systems of the modified and unmodified unwoven sheets, the dependence of the mean number of layers penetrated by the bullet on the time of the accelerated ageing process where the temperature was the only ageing factor, is presented in ***Figure 10***.

Along with the length of accelerated ageing, the average number of penetrated layers increased in, both systems of modified and unmodified sheets. Differences in the parameter between the systems assessed were statistically insignificant.

It should be noted that after the longest time of the accelerated ageing process, full piercing was observed in the model insert system of unmodified sheets.

Figure 11 presents the dependence of the mean value of deformation of the model insert systems made of modified and unmodified unwoven sheets assessed on the time of the accelerated ageing process where the temperature was the only ageing factor.

Research on the accelerated ageing of the insert systems where the only ageing factor was the temperature did not discover significant statistical differences in the mean value of the base deformation.

Under the testing conditions no significant changes in the mean number of perforated layers of unwoven sheets, both modified and unmodified, were observed during the accelerated ageing process where the temperature with humidity were the ageing factors (***Figure 12***).

When assessing the depth of base deformation, an insignificant decrease in its mean value was observed for the model insert systems made of unmodified sheets (***Figure 13***). When assessing the inserts made of modified unwoven sheets, no significant statistical changes were observed in the above parameter.

Conclusions

As part of works performed for confirmation of the stability of functional features, tests were executed to verify the ballistic resistance (fragment-proofness and bullet-proofness) of optimised model insert systems (consisting of textile materials, unmodified or modified) before and after the process of accelerated ageing.

Regarding the model insert systems made of p-aramid fabric subjected to modification or not, after the process of accelerated ageing with the temperature factor, similar change trends were discovered in the V50 – the parameter that determines the fragment-proofness. Significant alteration in the volume of the V50 parameter measured was identified after the first 28 days of accelerated ageing of ballistic model systems consisting in modified and unmodified p-aramid woven fabric systems with p-aramid wovens.

In another research variant where humidity was applied as an ageing factor in addition to the temperature, a distinct decrease in V50 (approx. 11% as compared to the initial value of V50 after 42 days of accelerated ageing) was discovered during accelerated ageing of the model insert systems produced of unmodified fabrics, which was lower by half (by approx. 5% as compared to the initial value) in the inserts designed with PACVD modified woven fabric.

The research confirms the stability of the material's functional parameters gained in the process of modification with low-temperature plasma at a level sufficient to observe a decrease in the dynamics of changes in the bullet-proofness in the inserts of modified fabrics.

The model insert systems made of modified or unmodified unwoven sheets of UHMWPE fibres exhibited a significantly different trend of changes in fragment-proofness when the temperature together with humidity were applied as the ageing factors. In the inserts made of modified unwoven sheets, an increase in the V50 value was observed, while the V50 of the inserts made of unmodified sheets decreased along with the extension of the accelerated ageing process.

Tests of the bullet-proofness according to the K2 class (of the PN-V-87000:2011 standard) did not show – it is worth emphasizing – any case of full piercing of the model insert systems made of textile materials subjected to low-temperature plasma modification in the presence of vapours of TDFH or HMDSO.

Among the insert systems made of unmodified materials based on either p-aramid fabrics or unwoven sheets of UHMWPE fibres, full penetration (piercing) with a projectile was observed in the samples after 42 days of ageing where the only aging factor was the temperature.

During the research on the number of perforated layers of the model insert systems subjected to the process of accelerated ageing, no statistically significant changes were observed in the inserts made of p-aramid fabrics, either modified or not. The same similarity was observed when assessing the deformation depth upon shooting. In the inserts made of unwoven sheets subjected to modification, the process of accelerated ageing conducted with either temperature alone or temperature with humidity did not significantly change the number of perforated layers nor the deformation depth, as compared to the results of tests performed on the model insert systems made of unmodified sheets.

In conclusion, it should be emphasised that modification with low-temperature plasma in the presence of vapours of low-molecular fluorine- or silane-genic substrates altered the properties of the fabrics and unwoven sheets. The above-observed phenomenon i.e. humidity is a more critical factor influenced the ballistic behaviour of the p-aramid woven fabric. Moreover PACVD modification allows to prevent the destructive influence of humidity during the ageing process.

References

1. Gonzales A, Schofield RB, Hart SV. Third Status Report to the Attorney General on Body Armor Safety Initiative Testing and Activities, 24.08.2005, U.S. Department of Justice Office of Justice Programs, National Institute of Justice http://www.ojp.usdoj.gov/bvpbasi/docs/SupplementII_08_12_05.pdf?popupWindow=Y; [2010-07-30].
2. NIJ Body Armor Standard Advisory Notice 01-2005, U.S. Department of Justice, 24.08.2005.
3. Struszczyk MH, Puszkarz AK, Miklas M, Wilbik-Hałgas B, Cichecka M, Urbaniak-Domagała W, Krucińska I. Effect of Accelerated Ageing on Ballistic Textiles Modified by Plasma-Assisted Chemical Vapour Deposition (PACVD). *FIBRES & TEXTILES in Eastern Europe* 2016; 24, 1(115): 83-88, DOI: 10.5604/12303666.1167429.
4. Struszczyk MH, Puszkarz AK, Wilbik-Hałgas B, Cichecka M, Litwa P, Urbaniak-Domagała W, Krucinska I. The Surface Modification of Ballistic Textiles Using Plasma-assisted Chemical Vapor Deposition (PACVD). *Textile Research Journal* 2014, 84, 19, 2085–2093
5. Struszczyk MH, Puszkarz AK, Wilbik-Hałgas B, Cichecka M, Litwa P, Urbaniak-Domagała W, Krucinska I. The Performance Stability of the 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.
6. Struszczyk MH, Puszkarz AK, Wilbik-Hałgas B, Cichecka M, Litwa P, Urbaniak-Domagała W, Krucinska I. The Surface Modification of Ballistic Textiles Using Plasma-assisted Chemical Vapor Deposition (PACVD). *Textile Research Journal* 2014; 84, 19, 2085-2093.
7. Struszczyk MH, Puszkarz AK, Miklas M, Wilbik-Hałgas B, Cichecka M, Urbaniak-Domagała W, Krucińska I. Effect of Accelerated Ageing on Ballistic Textiles Modified by Plasma-Assisted Chemical Vapour Deposition (PACVD). *FIBRES & TEXTILES in Eastern Europe* 2016, 24, 1(115): 83-88. DOI: 10.5604/12303666.1167429.

Received 14.09.2017 Reviewed 17.01.2018