

Effect of Accelerated Ageing on the Ballistic Resistance of Hybrid Composite Armour with Advanced Ceramics and UHMWPE Fibres

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Institute of Security Technologies MORATEX,
M. Skłodowskiej-Curie 3, 90-505 Łódź, Poland,
* e-mail: mfejdyś@moratex.eu

Abstract

The main objective of this complex study was to evaluate the durability of newly developed ballistic inserts designed using ultra-high-molecular-weight polyethylene (UHMWPE) fibres and advanced ceramics (Al_2O_3 or SiC). The forecasting of changes in the properties of the newly developed ballistic system is related to safe use and reliable construction, and requires ageing tests to be carried out in natural conditions. Due to the length of this process, a program of tests was developed for simulated use of the composite ballistic inserts under conditions of accelerated ageing, taking into account the 6-year lifespan of these products, which is in accordance with the PN-V-87000:2011 standard. As part of the research work, the new ballistic inserts were tested, and also ones subjected to laboratory ageing for 50, 100, 150 days, which corresponded to 2.2, 4.3 & 6.5 years of ageing in real conditions. The samples selected were verified in terms of ballistic and mechanical behaviour as well as changes in their chemical structure. Changes in the microstructure of the ballistic materials were evaluated using DSC analysis as well as infrared spectroscopy (FTIR-ATR).

Key words: accelerated ageing, ballistic system, ultra-high-molecular-weight polyethylene fibres (UHMWPE), hybrid composite.

Introduction

Ballistic resistant body armour is used by law enforcement officers, the military and others in various weather and climate conditions. Vests of this type are used in a variety of environments (temperature and humidity cycling) that may decrease the ballistic performance of the armour. One of the materials most widely applied for the manufacture of ballistic personal armours is ultra-high-molecular-weight polyethylene (UHMWPE) fibres due to their high strength, low density and superior fatigue resistance [1-3]. In addition to this material, several new composite materials have been introduced to improve ballistic armour performance, including hybrids consisting in fibre composites and ceramics [4-6]. Despite the intensive focus on ageing methodologies for composite armour materials over the last few years, there is not enough information about the influence of the environment on the ballistic behaviour of these composites. There is currently no protocol to determine if such degradation occurs, and if that is the case, how it should be measured. Several standards prescribe tests to study the performance of body armour articles at elevated temperatures, like the conditioning protocols of NIJ 0101.06 [7] or the temperature and climate tests of the standard for body armour [8]. Therefore, there is a need for methodologies which can be used to rapidly evaluate any newly developed materials and products in validated con-

ditions. Research on the performance of ballistic products exposed to the impact of external factors has been increasingly conducted in the last years. Chabba et al. [9] tested Dyneema® SK76, Dyneema® UD SB21, SB31 & SB61 under conditions of accelerated ageing. Analysis of the material properties tested proved that changes occurring inside the products during 8-weeks of ageing at a temperature of 65 °C and relative humidity of 80% correspond to those occurring in the same products under conditions of natural ageing for over 5 years at 35 °C. Based on this extrapolation, the test conditions correspond to a real ageing time of 5 years at 35 °C, which is considered a typical baseline requirement for ballistic resistant vests. Padovani et al. [10] published a study on ballistic articles based on Dyneema®, ultra-high-molecular-weight polyethylene (UHMWPE) fibres, that were subjected to real ageing and use. These products were ballistically tested according to the specifications used at the time of manufacture to verify the level of ballistic protection retention. The products were visually inspected and further tested according to relevant standards. The tests of V50 and examination of penetration/BFS (back face signature) were conducted. The results reveal that the products made of Dyneema® still showed a ballistic resistance similar to that at the stage of certification. The tests of V50 proved that Dyneema® SB retains ballistic resistance, as determined for the initial product. Meulman

[11] tested soft armour packages and hard armour panels at 70 °C, an extreme temperature for UHMWPE body armour, and immediately after conditioning they were submitted to V50 tests. These V50 tests showed that the performance of samples indicated a limited drop in V50. Using a simple model, the amount of material to compensate for this performance drop can be estimated. The results indicated that the system made of Dyneema® UD is capable of passing acceptance performance tests at elevated temperatures.

In the NISTIR report The National Institute of Justice (NIJ) described a process to define test requirements for a new NIJ standardisation document on body armour 7627 [12]. As part of their study on the conditions which ballistic resistant vests are subjected to daily when used by law enforcement officers, the temperature in cars used by the officers was measured. The highest temperature measured was 67 °C.

Fejdys et al. [13, 14] discussed the effect of ageing processes (real-time and accelerated) on the usage properties and safety of ballistic inserts made of Dyneema® SB21.

The aim of work [15] was to use accelerated tests, short exposures to weather and gamma radiation to study the influence of ageing agents on the mechanical and ballistic performance of UHMWPE composite armour. Composite panels were subjected to ballistic tests using 9 mm calibre projectiles. The mechanical and ballistic characteristics of the composite were related to macromolecular modifications induced in the polymer by the environment through physicochemical testing. Exposure to environmental agents induces changes in the UHMWPE macromolecular chains, altering the mechanical properties and ballistic behaviour of the composite. A number of studies have demonstrated that the external factors can change many of the physical and chemical properties of UHMWPE [16-19].

However, since ballistic composite armour, including hybrids consisting in fibre composites and ceramics, have been developed and commercialised only recently, there is not enough information about the influence of the environment on their ballistic behaviour. In consequence, there is a need for additional studies to improve our understanding of the performance of the hybrid compos-

ite mentioned under external conditions (different weather conditions).

In the development of guidelines and test methods for assessing the long-term performance of body armour it is critical not only to understand the microscopic and macroscopic ageing phenomena that lead to the performance degradation of these materials but also to verify the accelerated ageing methods that are used to make informed decisions on the selection of materials and accurately predict their long-term performance of new ones.

The aim of the research was to establish a validated research programme and conditions of accelerated ageing for newly developed ballistic protections made of a hybrid composition of ceramic and the UHMWPE fibrous composite.

This paper expands the subject and presents results up to the application level. Furthermore, the study performed makes the claim that the newly developed ballistic inserts retain their properties over a time-scale of at least 6 years and that the research methodology applied allows for durability verification of newly developed protective products.

■ Materials

The objects of the study were two types of ballistic inserts:

- soft ballistic inserts (WBM) made of Dyneema® SB51 – UHMWPE fibrous sheets,
- hard ballistic inserts made of multi-layer hot-pressed UHMWPE fibrous sheets (polyethylene plate WBT) and advanced ceramics (**Figure 1**) based on:
 - aluminium trioxide (Al₂O₃) (Barat Ceramics GmbH, Germany) with a thickness of 4.50 ± 0.01 mm and areal density of 26.0 ± 0.2 kg/m² (WBT I ballistic insert);
 - silicon carbide (SiC) (ESK Ceramics GmbH & Co. KG, Germany) with a thickness of 12.00 ± 0.01 mm and areal density of 44.0 ± 0.2 kg/m² (WBT II ballistic insert).

Soft ballistic inserts (WBM) were produced from UHMWPE fibrous sheets – Dyneema® SB51.

A polyethylene plate (WBT) was developed in the pressing process of UHMWPE fibrous Dyneema® HB26 sheets. The hot-pressing process was carried

out in several stages and encompassed initial hot-pressing (T = 130 °C), proper hot-pressing, (T = 130 °C) and cooling (T = 130 °C – 65 °C). A pressure of approx. 20 MPa was used in the hot-pressing. The multilayer hot-pressed UHMWPE plate (WBT) used in the construction of ballistic inserts WBT I and WBT II had the same structure and areal density – 12.0 ± 0.2 kg/m².

The ballistic elements, including advanced ceramics (Al₂O₃ or SiC) and WBT, were joined using silicone adhesive – Terostat MS 9399 (Henkel Poland/Poland). The WBT I and WBT II ballistic inserts were protected using suitable coatings, as shown in **Figure 2**.

The WBT I and WBT II hard ballistic inserts were used in conjunction with soft ballistic inserts (WBM) with an areal density of 6.0 ± 0.2 kg/m², showing ballistic resistance in line with the IIIA level of NIJ Standard 0101.04 and the K2 and O3 classes according to PN-V-87000:2011.

Research related to the development of WBM, WBT I and WBT II ballistic inserts was presented in [20].

■ Accelerated ageing

The inference regarding changes in the technical status of ballistic products under conditions of storage and usage requires testing based on the method of accelerated ageing, which assumes at least a 6-year lifespan of WBT I and WBT II ballistic inserts according to PN-V-87000:2011. The ballistic inserts were exposed to accelerated ageing for 50, 100 and 150 days, which corresponds to 2.2, 4.3 and 6.5 years of ageing in real conditions, respectively (the time of ageing was calculated according to a formula included in the ASTM F1980-07 Standard [21]). The test was carried out in a KBF 240 climatic chamber (BINDER GmbH/Germany). The ballistic products were exposed to the impact of raised temperature of 70 ± 0.5 °C and humidity of 0 + 1.5%.

■ Testing methods

Mechanical properties

Mechanical properties of the Dyneema® SB51 sheets were tested before and after accelerated ageing according to PN-EN ISO 1421/1:2001 [22]. Measurements of the hardness of the polyethylene plate

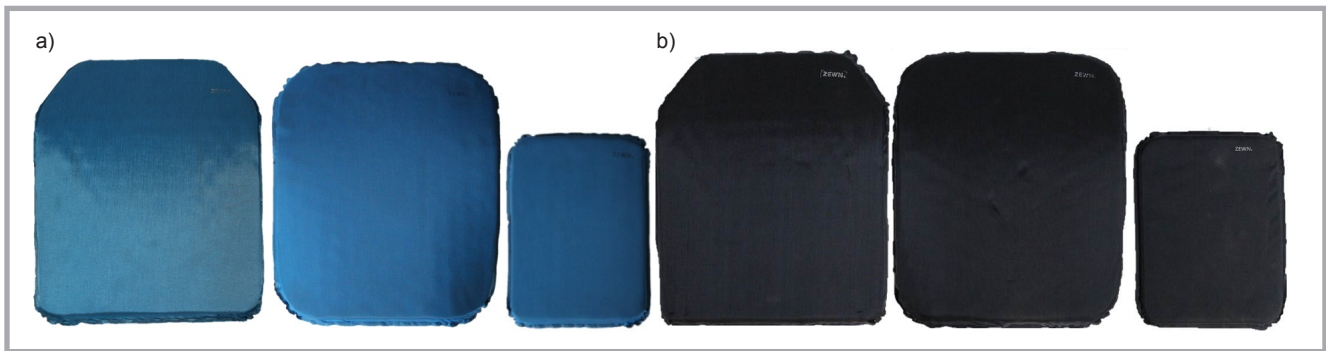


Figure 1. Hard ballistic inserts (front, back, side): a) WBT I ballistic inserts, b) WBT II ballistic inserts.

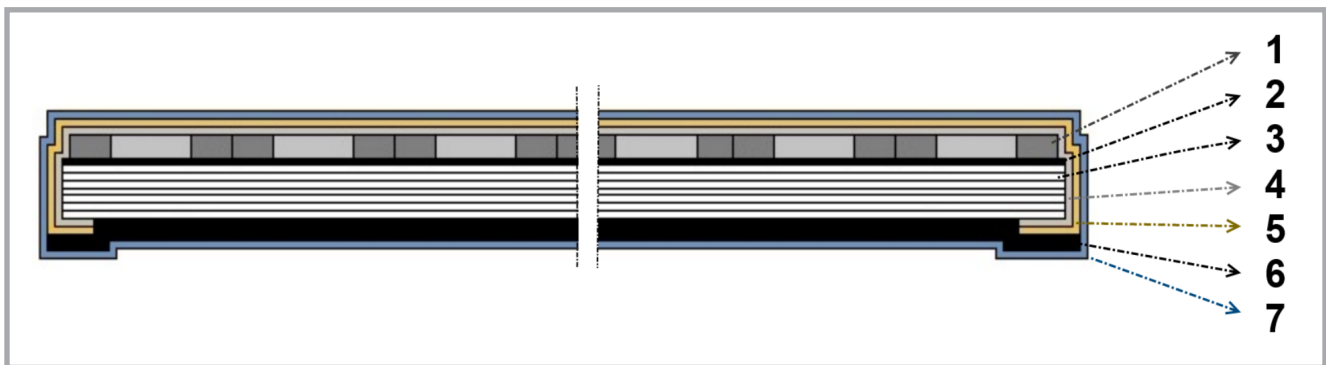


Figure 2. Idea of hard ballistic insert: 1 – ceramic layer, 2 – adhesive layer, 3 – polyethylene plate (WBT), 4 – shock-absorbing and protective coating, 5 – anti-splintering coating, 6 – anti-diffraction foam, 7 – water-repellent fabric.

(WBT) were performed before and after the accelerated ageing tests using the Rockwell method as per PN-EN ISO 2039-2 [23]. Tests on the polyethylene plate (WBT) were conducted by making 7 prints on a selected surface using a ball with a diameter of 6.35 mm at a load of 980.7 N. Hardness measurement of the advanced ceramics (Al_2O_3 , SiC) mechanically separated from other components of the insert was performed using a method (Vickers) as per PN-EN ISO 843-4 [24], applied before and after the ageing cycles. Samples for measurement were prepared by separating the adhesive residue from the polyethylene plate and advanced ceramics, then the testing surface of the plate and ceramics was re-sanded and polished to achieve a roughness of $R_a \leq 0.05 \mu\text{m}$.

Ballistic properties

The ballistic resistance of the ballistic inserts (WBM, WBT I and WBT II) was measured in accordance with PN-V-87000:2011 [8]. The ballistic inserts were tested for their P/BFS (Penetration/Back Face Signature) performance against:

- a 7.62×25 mm FMJS projectile with an impact velocity of 420 ± 15 m/s (WBM ballistic insert);

- a 5.56×45 mm SS109 projectile with an impact velocity of 950 ± 15 m/s (WBT I ballistic insert);
- a 7.62×51 mm AP projectile with an impact velocity of 820 ± 15 m/s (WBT I ballistic insert).

The samples were conditioned at elevated temperatures, then P/BFS tests were conducted immediately after their removal from the conditioning room, and finally it was verified whether the samples fulfilled the requirements of body armour standards [8]. P/BFS was evaluated after shooting using Weible Plasticine modelling clay placed behind the armour system; the trauma in the clay duplicated the transient deformation of the composite armour on the back of the system.

ATR-FTIR

FTIR (Fourier transform infrared spectroscopy) of the Dyneema® SB51 sheets and polyethylene plate (WBT) were made using a NICOLET IS10 spectrophotometer (Thermo Scientific) with ATR (Attenuated Total Reflection) reflective technology in the range of $400\text{--}4000 \text{ cm}^{-1}$. The starting point for the test using the ATR-FTIR technique was

cutting out a sample with dimensions of 20×20 mm and placing it on the crystal, clamping it properly. In order to perform the test, two measurements were carried out: the background spectrum, i.e. the crystal alone, and spectrum of the crystal with the sample. Measurement of the background was recorded in the internal memory of the spectrophotometer and automatically subtracted upon measurement of the sample. This way, the impact of external conditions on test results was eliminated.

Assessment of thermal properties using differential scanning calorimetry (DSC)

Thermal analysis of the Dyneema®SB51 sheets and polyethylene plate (WBT) was carried out in an inert nitrogen gas atmosphere using a differential scanning calorimeter by Mettler Toledo. A sample with a mass of $8 \div 10$ mg was placed in a thermal analyser furnace and heated at a rate of $10 \text{ }^\circ\text{C}/\text{min}$ to a temperature of $180 \text{ }^\circ\text{C}$. The sample was kept at this temperature for 5 minutes, then cooled down to a temperature of $-60 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C}/\text{min}$. Then it was reheated to $180 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C}/\text{min}$. Based on the DSC curves, the phase transition

Table 1. Results of breaking load tests for the Dyneema® SB51 sheet before and after 50, 100 and 150 days of accelerated ageing.

Duration of accelerated ageing, days	Dyneema® SB51 sheet			
	Tensile strength, N		Elongation at break, %	
	Lengthwise	Crosswise	Lengthwise	Crosswise
0	9121±413	9001±275	5.3±0.2	6.0±0.5
50	7805±383	8751±410	6.1±0.2	5.5±1.1
100	7757±816	8605±783	5.6±0.5	5.4±0.3
150	7000±119	8247±453	4.9±0.9	5.4±0.7

Table 2. Hardness testing of materials used in the ballistic inserts subjected to accelerated ageing cycles.

Type of sample	Duration of accelerated ageing, days	Rockwell hardness	Vickers hardness
polyethylene plate WBT	0	26.4 ± 2.58	-
	50	12.6 ± 2.61	
	100	25.2 ± 1.92	
	150	26.4 ± 2.65	
advanced ceramics Al ₂ O ₃ (a component of ballistic insert WBT I)	0	-	16.67 ± 0.45
	50		15.46 ± 0.69
	100		15.84 ± 1.00
	150		16.34 ± 0.63
advanced ceramics SiC (a component of ballistic insert WBT II)	0	-	27.07 ± 0.84
	50		27.20 ± 0.64
	100		26.63 ± 0.85
	150		26.93 ± 0.99

temperatures of the test material and the crystallinity index of the test materials were determined according to the **Equation (1)** [14]:

$$x_c = \frac{\Delta h_m}{\Delta h_m^0} * 100\% \quad (1)$$

x_c – degree of crystallinity;

Δh_m – enthalpy connected with the melting process of the crystalline phase;

Δh_m^0 – enthalpy connected with the melting process of the crystalline phase PE, completely crystalline ($\Delta h_m^0 = 293$ J/g).

Statistical analysis

The results of the research were subjected to statistical analysis using Student's t test. For a confidence level of 0.95 and respective degree of freedom, there were confidence intervals established for the average value. On that basis some of the data exceeding the scope of the intervals were rejected. The hypothesis concerning the compatibility of the average results achieved for selected time-periods with a double number of tests was verified. The statistic value of t_{obl} was calculated according to the following **Equation (2)**:

$$t_{obl} = \frac{|x_1 - x_2|}{\sqrt{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}} \sqrt{\frac{n_1 n_2 (n_1 + n_2 - 2)}{n_1 + n_2}} \quad (2)$$

x_1, x_2 – arithmetical means of results achieved for selected time-periods with a double number of tests,

n_1, n_2 – number of results achieved for selected time-periods with a double number of tests,

S_1^2, S_2^2 – variances obtained for results achieved for selected time-periods with a double number of tests.

In this specific case, the value of t_{obl} was lower than the one in the Student's t ratio in the tables; therefore the difference between the results was related to random errors only. Thus, the validation procedures were as good as the reference ones [25].

Results and discussion

Analysis of mechanical properties

The progress of ageing was evaluated for Dyneema® SB51 sheets and a polyethylene plate (WBT). Samples of Dyneema® SB51 were tested for the effects of the breaking load in accordance with PN-EN ISO1421/1:2001 before and after 50, 100 and 150 days of accelerated ageing. Results of the tests are presented in **Table 1**.

In the case of Dyneema® SB51 sheets intended for the production of soft ballis-

tic inserts (WBM), after 50, 100 and 150 days of accelerated ageing, a gradual decrease in the breaking load was observed as compared to the value of the breaking load of the samples which had not been subjected to the laboratory ageing cycles, which was, respectively, 14%, 15% & 23% (lengthwise) and 3%, 4% & 8% (crosswise).

The results show that much smaller declines in the value of the breaking load followed in the case of Dyneema® SB51 sheets in the crosswise direction.

The progress of the accelerated ageing was also assessed for a multi-layer, hot-pressed UHMWPE fibrous composite and polyethylene plate (WBT), through hardness tests before and after the accelerated ageing in accordance with PN-EN ISO 2039-2: 2002 (Rockwell hardness). Moreover, the hardness of ceramics applied in the WBT I and WBT II inserts was examined according to PN-EN ISO 843-4:2007/P (Vickers hardness), the results of which are shown in **Table 2**.

In the tests carried out on WBT samples subjected to accelerated ageing for 50 days, a reduction in hardness of approximately 50 % was observed as compared to the polyethylene plate (WBT) not subjected to ageing. Following a significant reduction in the hardness of the WBT sample after 50 days of ageing, we can observe a significant increase in the hardness of the polyethylene plate samples aged for 100 and 150 days. The significant reduction in the hardness of the WBT sample after 50 days of ageing may be the result of a large number of defects which appear on the surface of the sample, which lost the ability to transfer tension into the material. This variation in hardness values may be the result of alternatively occurring processes i.e. the breakdown of polymer chains, oxidation and cross-linking [13]. The UHMWPE-based composites subjected to accelerated ageing in the initial stage show a significant increase in the value of mechanical properties (e.g. hardness) compared to the initial value of a given property, whereupon a decrease in the mechanical value comes after reaching its maximum. Similar behaviour of polyethylene materials was observed by Tidjani A. [26, 27], Bernède J. C. [28] and Rabello M. S. [29]. When evaluating the mechanical properties of UHMWPE-based materials subjected to accelerated aging at specific exposure times, it

can be observed that after an initial deterioration, they improve in the course of further ageing. Such a variability of mechanical properties is linked with parallel processes of oxidation and cross-linking of polymer chains, or this effect is attributed to the appearance of a significant number of defects on the surface of the sample, which loses its ability to transfer stresses deep into the material.

Based on the results obtained, minimal changes were found in the hardness of advanced ceramics Al_2O_3 with a thickness of 4.5 mm and SiC with a thickness of 12 mm, subjected to accelerated ageing for 50, 100 and 150 days.

Ballistic properties assessment

Ballistic tests of soft ballistic inserts (WBM) developed on the basis of Dyneema® SB51 and a ballistic system containing WBM and hard ballistic inserts – a hybrid composite made of WBT and advanced ceramics (Al_2O_3 – WBT I or SiC – WBT II), were carried out in accordance with the requirements of PN-V-87000:2011 in dry conditions. The results of ballistic tests are presented in **Table 3**.

The statistical studies show that the ballistic inserts (WBM, WBT I, WBT II) which were subjected to accelerated ageing retained their ballistic properties and fulfilled the proposed assumptions of the PN-V-87000:2011 standard.

The studies showed that in the case of soft ballistic inserts (WBM) subjected to accelerated ageing for 50, 100 and 150 days, there is no significant difference between the values of the mean substrate deflection (BFS) as compared to the results obtained for ballistic inserts which had not been subjected to conditioning cycles, as illustrated in **Figure 3**. However, the results of ballistics studies of ballistic systems WBT I and WBT II show that a temperature of + 70 °C, which the ballistic insert is exposed to in the initial phase of the ageing process, improves the ballistic properties, manifested as a decline in the value of the mean substrate deflection (BFS). Then in the course of further ageing of WBT II, there is an increase in this value. Such behaviour of the insert tested may be the result of the overlapping effects of different ageing processes, such as chain cracking (leading to an increase in the value of BFS), branching and cross-linking (decrease in BSF).

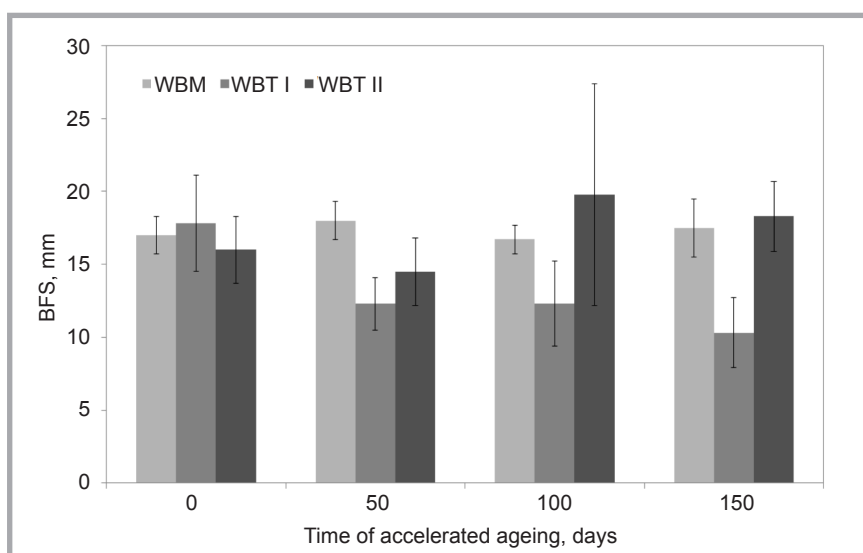


Figure 3. Effect of accelerated ageing on the backface signature (BSF) of ballistic inserts.

Infrared spectroscopy ATR-FTIR

Structural studies by FTIR-ATR infrared spectroscopy in the range 400-4000 cm^{-1} were carried out before and after the ageing cycles applied for:

- Dyneema® SB51 sheet,
- polyethylene plate WBT.

Analysis of ATR-FTIR tests of the Dyneema® SB51 sheet after 50, 100 and 150 days of accelerated ageing showed a slight increase in the intensity of bands in the wavenumber range of 1615 to 1750 cm^{-1} (**Figure 4**), corresponding to the vibrations of atoms of carbonyl groups C=O. The largest absorption increase for carbonyl groups was observed after 150 days of accelerated ageing. In the process of thermally initiated degradation which occurs with the participation of oxygen from the air, an essential element of changes to the structure of

polymer chains is their oxidation, resulting in the formation of carbonyl groups of the acid, ketone, ester and per-acid type [13, 14]. The increase in the intensity of bands in the wavenumber range of 1615-1750 cm^{-1} indicates structural changes occurring in macromolecules under the influence of the conditions of accelerated ageing applied, resulting in the breakdown of chains, which leads to a reduction in the molecular weight of polyethylene and causes the deterioration of mechanical properties (decrease in the value of the breaking load of the Dyneema® SB51 sheet of 23% in the longitudinal direction after 150 days of accelerated ageing and 8% in the transverse direction).

The polyethylene plate (WBT) is made of multilayer hot-pressed UHMWPE fibrous sheets of Dyneema HB26. In Dyneema HB26 sheets a matrix is a pol-

Table 3. Ballistic resistance of ballistic inserts subjected to accelerated ageing. *Note:* m – bullet mass, V – velocity of projectile.

Type of ballistic insert	Reference document/ resistance class	Duration of accelerated ageing, days	Ammunition type	Average backface signature, BFS, mm
WBM	PN-V-87000:2011/K2	0	7.62 × 25 mm FMJS $m = 5.5 \pm 0.1$ g $V = 420 \pm 15$ m/s	17.0 ± 1.3
		50		18.0 ± 1.3
		100		16.7 ± 1.0
		150		17.5 ± 2.0
WBT I (used in conjunction with WBM)	PN-V-87000:2011/K3	0	5.56 × 45 mm SS109 $m = 4.0 \pm 0.1$ g $V = 950 \pm 15$ m/s	17.8 ± 3.3
		50		12.3 ± 1.8
		100		12.3 ± 2.9
		150		10.3 ± 2.4
WBT II (used in conjunction with WBM)	PN-V-87000:2011/K5	0	7.62 × 51 mm AP $m = 9.7 \pm 0.1$ g $V = 820 \pm 15$ m/s	16.0 ± 2.3
		50		14.5 ± 2.3
		100		19.8 ± 7.6
		150		18.3 ± 2.4

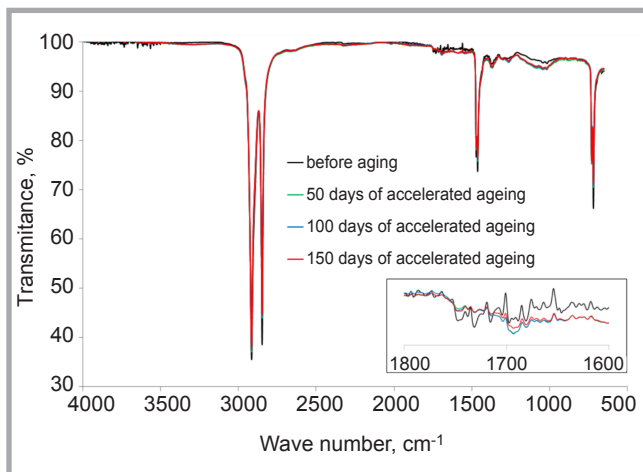


Figure 4. ATR-FTIR spectra of the Dyneema® SB51 sheet before and after accelerated ageing.

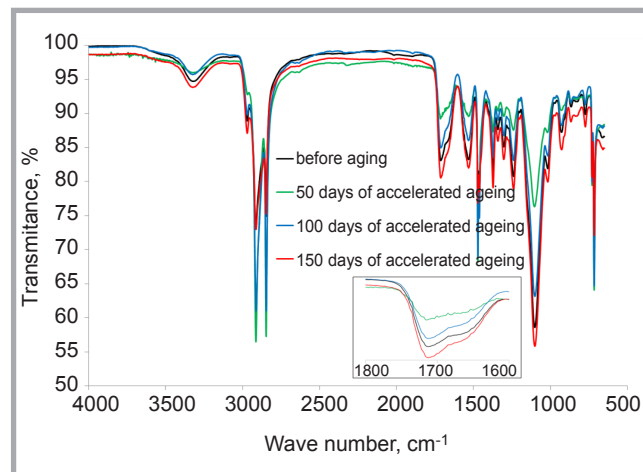


Figure 5. ATR-FTIR spectra of the polyethylene plate (WBT) before and after accelerated ageing.

Table 4. Results of DSC analysis of the Dyneema® SB51 sheet and polyethylene plate WBT in an inert gas (nitrogen) atmosphere. **Note:** T_m – melting point of crystalline phase, ΔH_m – enthalpy connected with the melting process of the crystalline phase, T_c – temperature of crystallisation; ΔT_c – temperature range of crystallisation, ΔH_c – enthalpy connected with crystallisation process; X_c – degree of crystallinity.

Sample	Duration of accelerated ageing, days	First heating			Cooling		Second heating		
		T_m , °C	ΔH_m , J/g	X_c , %	T_c , °C	ΔH_c , J/g	T_m , °C	ΔH_m , J/g	X_c , %
Dyneema® SB51 sheet	0	123; 148; 151; 153	211	72	116	124	136	139	48
	50	123; 150	207	71	116	117	136	140	48
	100	124; 151; 152	196	67	116	111	136	133	46
	150	124; 149; 152; 153	217	74	116	124	136	146	50
polyethylene plate WBT	0	139; 152; 156; 159	204	70	117	104	137	118	40
	50	139; 152; 156; 159	204	70	117	102	137	117	40
	100	139; 150; 152; 158	206	70	117	102	137	119	41
	150	139; 153; 155	197	67	117	99	137	112	38

urethane composition formed by the reaction of an aliphatic diisocyanate and aliphatic polyether diols [30]. Thus, in the ATR-FTIR spectra of the polyethylene plate (WBT), shown in **Figure 5**, the absorption bands within the range of wavenumbers 1700 cm^{-1} , 1520 cm^{-1} & 1096 cm^{-1} are observed specifically for polyethylene resulting from the vibrations of bonds OCO, CONH and COC.

The ATR-FTIR spectra of the polyethylene plate (WBT) showed a decrease after 50 and 100 days of accelerated ageing in the intensity of bands corresponding to:

- CH_2 (1370 cm^{-1});
- OCH_3 (1335 cm^{-1});
- OC(=O)NH , CH_2 (C-H, rocking and twisting) (1305 cm^{-1});
- NH , OH (3300 cm^{-1});
- C=O (1700 cm^{-1});
- COC (1072 cm^{-1} , 1015 cm^{-1});
- C=N , NH , (1528 cm^{-1} , 1245 cm^{-1})

while there was an increase in the intensity of bands at 2915 cm^{-1} , 2845 cm^{-1} , 1470 cm^{-1} and 715 cm^{-1} corresponding to atom vibrations of CH.

However, in a sample subjected to accelerated ageing for 150 days, the above-described changes, related to the intensity of the bands examined, were reversed.

The analysis above indicates that in the case of the samples subjected to accelerated ageing for 150 days, intensive processes of thermal degradation had already begun in the material tested. Thermal degradation of the polyethylene plate (WBT) is a radical process, resulting in the detachment of hydrogen atoms of CH_2 in the main polymer chain and the formation of macroradicals. In addition to the processes of cracking of the main polymer chain, the presence of carbonyl groups in the polyethylene plate (WBT) also aids the breakdown of chains, initiated by temperature, into free radicals (initiation), caused by the detachment of oxygen atoms.

Assessment of thermal properties using differential scanning calorimetry (DSC)

The process of ageing was evaluated based on the thermal properties of

Dyneema® SB51 sheets and the polyethylene plate WBT. DSC analysis is presented in **Table 4**.

DSC curves of the Dyneema® SB51 sheet and polyethylene plate (WBT) are presented in **Figures 6** and **7**.

During the discussion on the results, it was important to show the thermal characteristics of two different UHMWPE-based materials: Dyneema SB51 (**Figure 6**), on the basis of which the WBM insert was designed, and Dyneema HB26 (**Figure 7**), on the basis of which the WBT insert was designed. DSC curves after each time interval are shown separately due to the fact that under the conditioning parameters applied, changes in the material tested occur not only in the degree of crystallinity, but also in the crystalline structures constituting the crystalline phase of the polyethylene material. Therefore, overlaying the DSC graphs on each other would not allow full visualisation of the changes occurring in the crystalline structure of the composite tested.

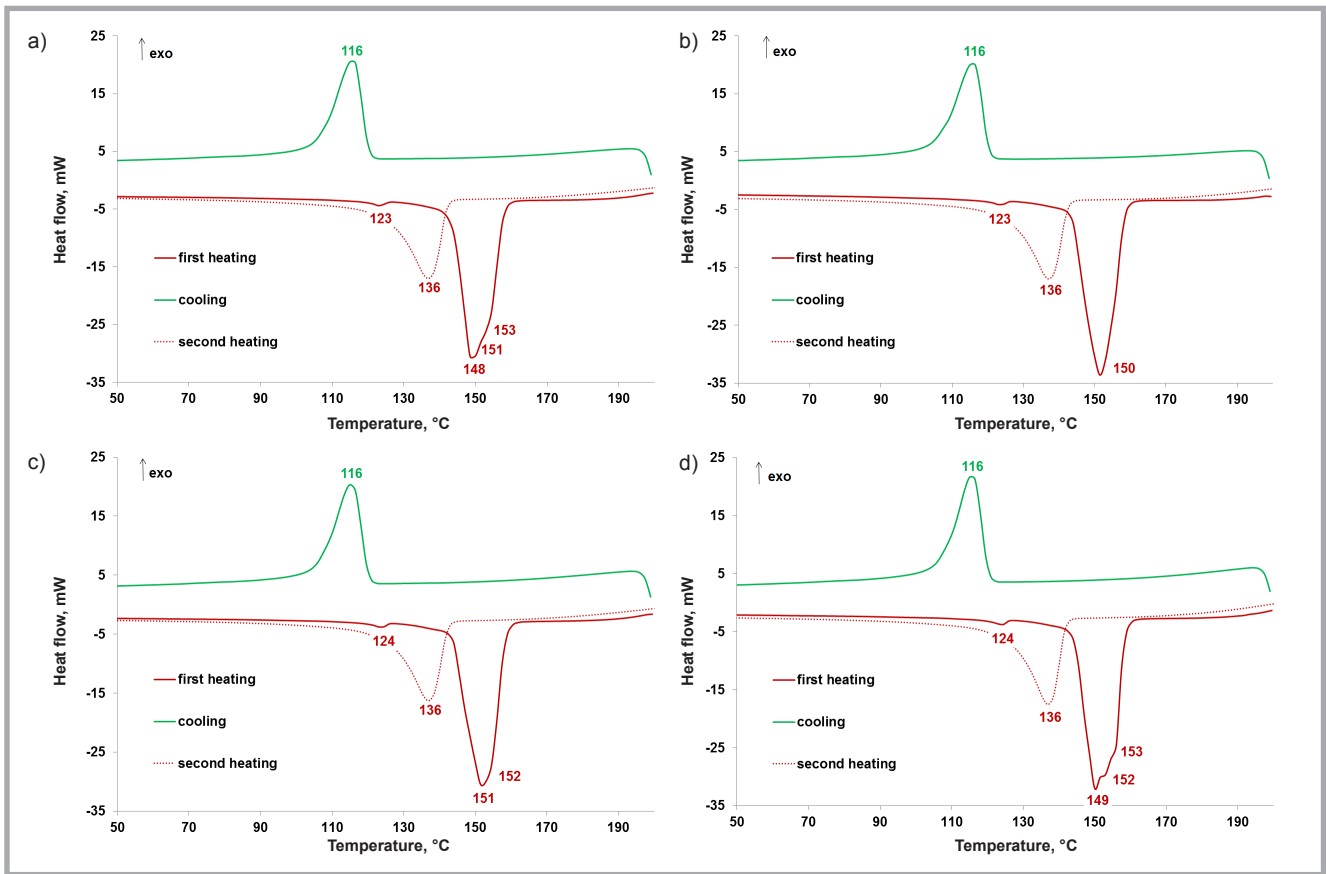


Figure 6. DSC curves of the Dyneema® SB51 sheet: a) before ageing, b) after 50 days of accelerated ageing, c) after 100 days of accelerated ageing, d) after 150 days of accelerated ageing.

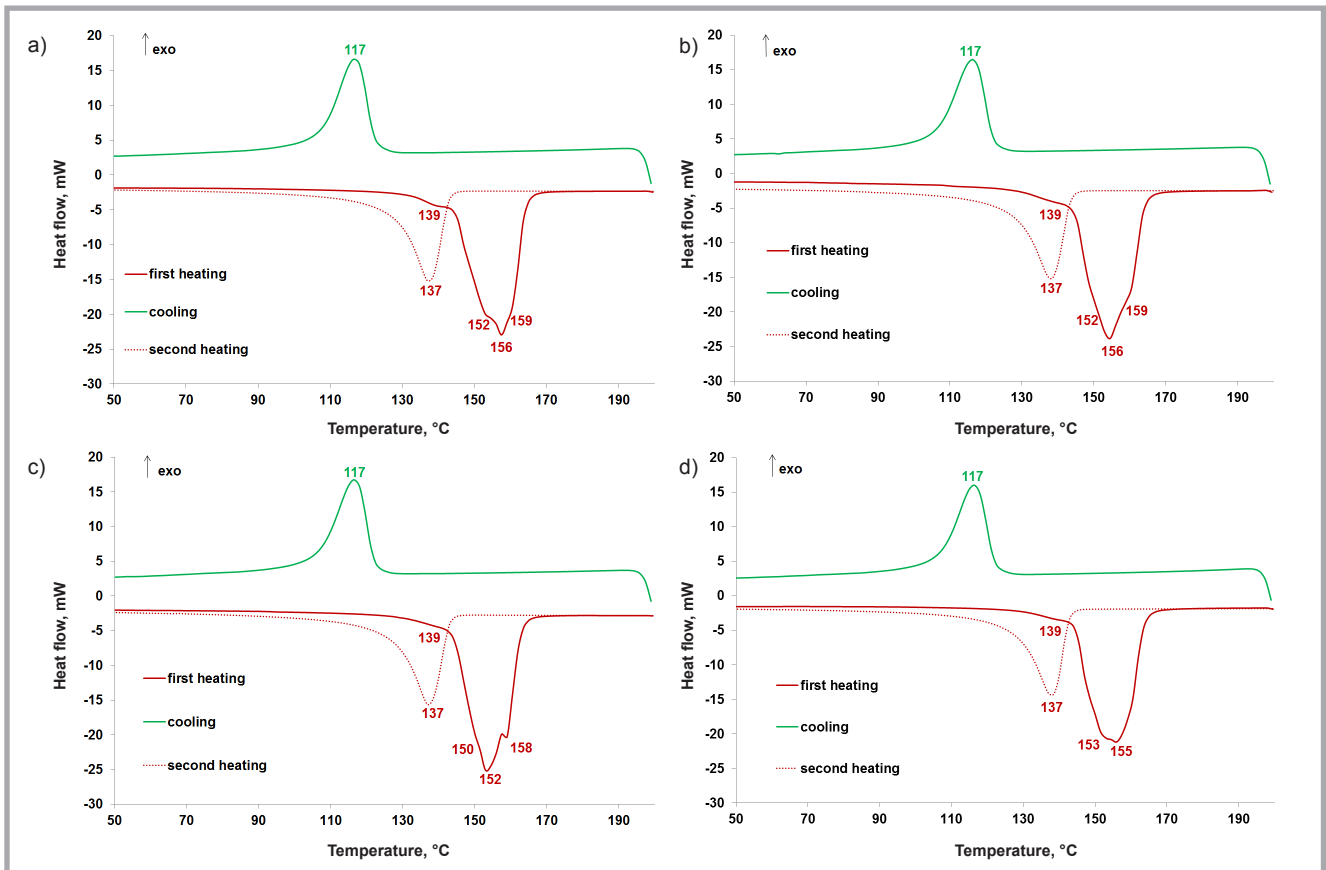


Figure 7. DSC curves of the polyethylene plate (WBT) a) before ageing, b) after 50 days of accelerated ageing, c) after 100 days of accelerated ageing, d) after 150 days accelerated ageing.

Analysis of the thermal effects of the Dyneema® SB51 sheet showed that this material both before and after exposure to accelerated ageing has a crystalline phase encompassing various crystalline structures. During the first heating, DSC endothermic peaks of the Dyneema® SB51 sheet subjected to ageing are assigned to the melting of the following crystalline structures [14]:

1. rhombic crystals – melting point: 147-152 °C;
2. pseudo-hexagonal mesophase – melting point: 153-159 °C.

Furthermore, on DSC curves during the first heating, a peak coming from the crystalline structure with a melting point of 123-124 °C was observed. It can be assumed that the presence of this peak on the DSC curve is related to the presence of the crystalline phase of the low-molecular polyethylene [14]. In the course of DSC applied to the Dyneema® SB51 sheet, during the second heating, an endothermic peak is observed, originating from the melting of corrugated lamellas at a temperature of approx. 135-137 °C, while there are no peaks observed originating from the crystalline forms which appear during the first heating. It can be assumed that during the second heating of the Dyneema® SB51 sheet at a constant rate, the process of unifying the crystalline structure of the material occurred. Based on the tests conducted, there is a noticeable change in the nature of the crystalline phase of aged samples compared to the Dyneema® SB51 sheet which was not subjected to accelerated ageing. The DSC method was used to calculate X_c of the Dyneema® SB51 sheet which was not subjected to the effect of laboratory ageing, the results of which are presented in **Table 4**. The experimental data show that the ageing processes occurring in the samples tested remarkably affect the change in X_c . X_c of the Dyneema® SB51 sheet aged under the accelerated conditions varies depending on the testing time. It decreases with an increasing ageing time, but it is not a linear relationship, since after 150 days of ageing, corresponding to 6.5 years of ageing in real conditions, an increase in X_c can be observed, which may be due to the reactions of branching and cross-linking occurring in the test material. These phenomena compete with the reactions of chain breakdown. The increase in X_c of the Dyneema® SB51 sheet after 150 days of ageing may also be caused by degradation processes occurring in

the amorphous regions, resulting in the breakdown of polymer chains, which can indirectly contribute to their ordered arrangement and, therefore, to the increase in X_c of the sample.

For the polyethylene plate (WBT), made of multilayer hot-pressed Dyneema® HB26 sheets, during the first heating, DSC endothermic peaks of the test samples are assigned to the melting of the following crystalline structures [14]:

- corrugated lamellas – melting point: 135-139 °C;
- rhombic crystals – melting point: 147-152 °C;
- pseudo-hexagonal mesophase: – melting point 153-159 °C.

During the second heating, an endothermic peak is observed, originating from the melting of corrugated lamellas at a temperature of 137 °C, while there are no peaks observed originating from other crystalline forms that appear during the first heating. It can be assumed that during the second heating of samples at a constant rate, the process of unifying the crystalline structure of the Dyneema® HB26 sheet occurred, which is also observed for the Dyneema® SB51 sheet. The course of DSC thermograms and a detailed analysis of thermal effects showed that in the polyethylene plate (WBT) produced, along with the progress of ageing, the crystalline phases change only slightly, which may be a sign of the high stability and resistance of the composite with respect to ageing. A change in the nature of the crystalline phase of the aged polyethylene plate (WBT) can be observed only for the sample subjected to accelerated ageing for 150 days, which corresponds to 6.5 years of ageing under natural conditions. This demonstrates that intense processes of thermal degradation had already begun to occur in the test material, which led to changes in the structure of polymer chains of the polyethylene. The experimental data show that the ageing time of the polyethylene plate (WBT) also affects, to a negligible extent, the change in its X_c , the values of which are shown in **Table 4**. X_c of the polyethylene plate (WBT) not subjected to accelerated ageing for 50 or 100 days has a value of 70%. In the case of WBT subjected to accelerated ageing for 50 and 150 days, an increase in X_c to a value of 67% was found. This is due to the fact that in the composite subjected to ageing for 150 days, the reactions of the degradation already occur, causing

the breakdown of chains, which results in a reduction in X_c .

■ Conclusions

The main objective of the research work was to confirm the thesis that the recently developed ballistic inserts with ceramic elements embedded into their structure retain their usage properties for a 6-year period at least, and that the method of research applied i.e, accelerated ageing along with structural and mechanical tests, allows to verify the sustainability of the recently developed protective products.

These studies were important in terms of the operational safety and structural reliability of the ballistic inserts developed, as well as for confirmation of the assumed service life (6 years). The period of persistence of a ballistic product is defined by the PN-V-870000:2011 Standard, assuming at least a 6-year period of service life. Therefore, research of the simulated ageing of the product developed was elaborated with that period in mind. An important assumption was confirmation of the permanence of parameters related to the ballistic protection capability of the product. Additional analysis of mechanical properties additionally confirmed that within the assumed period of use, the product will not change its usage properties.

Results of the structural, mechanical and ballistic research confirmed that the ballistic inserts developed (WBM, WBT I, WBT II) do retain their usage properties for a period of 6 years. Moreover, the developed and validated methodology of research on the accelerated ageing of hard ballistic inserts with ceramic elements embedded into their structure allows to estimate and verify the assumed lifetime of this type of ballistic product. The statistical studies show that the ballistic inserts (WBM, WBT I, WBT II) which were subjected to accelerated ageing for 50, 100 and 150 days, which corresponded to 2.2, 4.3, and 6.5 years of natural ageing, retained their ballistic properties. However, only evaluation of the mechanical parameters and structure of the materials applied in the inserts tested allowed to assess the impact of the accelerated ageing processes.

The impact of the ageing factors, progressing with the time of exposure, resulted in the deterioration of mechanical

properties and changes in the structural properties of Dyneema® SB51 sheets, used in the WBM ballistic insert (WBM) and polyethylene plate, developed on the basis of Dyneema® HB26 (a component of WBT I and WBT II ballistic inserts). Despite this, Dyneema® SB51 continued to fulfil the requirements set at the design stage in terms of tensile strength. In the case of tests carried out on samples of the UHMWPE fibrous composite used in WBT I and WBT II, even though in the assessment of mechanical properties we observed a reduction in hardness of approx. 50% after accelerated ageing for 50 days as compared to the sample not subjected to ageing, the nature of these changes is rather superficial, since neither DSC nor ATR-FTIR studies confirm the changes in the structure of this composite. Minor changes in the structure of the composite occurred only for samples subjected to ageing for 150 days, which was manifested in a slight decrease in Xc. These changes are primarily caused by variations in the chemical structure of macromolecules, which is confirmed by the increase in the intensity of absorption bands resulting from C=O groups in the ATR-FTIR spectra. In the case of the ceramic material applied, there was no change in its hardness with the progress of accelerated ageing. The types of advanced ceramics applied, based on Al₂O₃ or SiC, retained stability of mechanical properties under the conditions of ageing. Analysis of mechanical, ballistic and structural properties of the newly developed ballistic inserts made it possible to predict the correlation between the parameters of articles which will be subject to standard operation in the future (ageing in real time), and model processes conducted in accelerated time. In line with the objective of the experiment, a time interval was set after which change occurs in the test properties of the materials used to produce the ballistic inserts, which de facto allows for evaluation of the functionality and safety of the newly developed hybrid composites in terms of their suitability for use.

Accelerated aging studies assumed for 6 years should be treated in relation to the assessment of the durability of a composite product as a whole. Determining the critical ageing time after which a change occurs in the property tested by a certain value that affects the product's protective capabilities, required the determination of time intervals after which it was possible to precisely determine the deteriora-

tion of usage properties. In our case, the results obtained from hardness, and ballistic (BFS) and additional structural tests (FTIR and DSC) show that under the influence of the given conditioning conditions, intensive ageing processes take place in the inserts produced related to the reactions of breaking, oxidation and crosslinking processes of polymer chains, as indicated by the decrease or increase in the values of the parameters tested. Therefore, the reduction in BFS associated with the alleged improvement of ballistic properties during the ageing process indicates the intensive ageing processes in the composites tested, consisting in the simultaneous occurrence of the reactions of the breaking, oxidation and crosslinking of polymer chains.

In view of the above data, it can be concluded that the assessment of risk associated with the loss of performance and parameters responsible for the safety of protective products during the service time becomes an important issue, especially in terms of user safety. Therefore, it seems necessary to undertake studies of ballistic products under conditions of accelerated ageing and extend the knowledge in this field. The method of accelerated ageing testing used in this case and the results obtained can successfully provide guidance for changes in the current PN-V-87000:2011 and in other standards used to assess the protective properties of ballistic products, including the methods for testing the impact of ageing processes.



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Contact:

INSTITUTE OF BIOPOLYMERS AND CHEMICAL FIBRES
ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland
Natalia Gutowska, Ph.D.
e-mail: nls@ibwch.lodz.pl, n.gutowska@ibwch.lodz.pl