Marzena Fejdyś,
Magdalena Cichecka,
Marcin Łandwijt,
Marcin H. Struszczyk

Institute of Security Technologies „MORATEX”
ul. M Skłodowskiej-Curie 3, 90-505 Łódź, Poland
E-mail: mfejdys@moratex.eu

Prediction of the Durability of Composite Soft Ballistic Inserts

Abstract
The main goal of this research was to develop a method of predicting the durability of soft ballistic inserts made of a high-strength composite based on polyethylene ultra-high molecular weight (UHMWPE) fibres. The research presents a program of tests on the simulated use of composite ballistic inserts elaborated in order to predict the durability as well as changes in the ballistic, physical and mechanical properties occurring due to conditions of use. The research program took the following three procedures of the aging simulation of the ballistic inserts into account: procedure 1 – applying a mechanical load to the insert; procedure 2 – applying a mechanical load along with a temperature cycle to the insert; procedure 3 – applying a mechanical load, temperature cycle and liquid solution simulating human perspiration to the insert. The procedures were verified experimentally by examining inserts made out of soft composite polyethylene Dyneema® SB 21. Also verification by means of the Snedecor's F-test was carried out. It was shown that the effect of mechanical loading, temperature cycling, and the solution simulating human perspiration influences the progress of degradation of the polyethylene material. The research work included testing new ballistic inserts made of a polyethylene composite, as well as ones subjected to simulation ageing. To investigate the correlation between the natural ageing process and the simulated one, ballistic inserts used under natural conditions for 5, 7, 9 and 13 years were examined. Selected samples were used for the determination of mechanical and ballistic property variation as well as changes in their chemical structure. Changes in the microstructure of the ballistic material were assessed by DSC analysis and infrared spectroscopy (FTIR-ATR).

Key words: *simulation of use, accelerated ageing, ballistic protection, bullet-proof vests, fragment-proof vests, ballistic protection, ultra-high molecular weight polyethylene, crystallinity.*

Introduction

Ballistic products, as any other product for technical application, undergo gradual degradation with the passing of time. The main reasons are, inter alia, operating conditions, and the usage and storage procedures of ballistic products. The property change predictions of ballistic products are related to the security usage and reliability of the design, as well as the execution of ageing tests required under natural conditions. Due to the long duration of the process, methods of accelerated ageing of materials were used. The results obtained provide a basis for ageing research for further analysis based on selected mathematical methods allowing an adequate description of the phenomena related to ageing. The simulation of changes in the characteristics of the product tested, conducted with the use of selected prediction methods, is intended to determine the extent of change in these properties over a period longer than that of the test duration presumed [1, 2].

Most often the subjects of predictions are changes in basic physical properties (e.g., mechanical) as well as structural changes in the material caused by the ageing process [3 - 7]. Because of the importance of users' safety, more and more attention is paid to the prediction of the life cycle as well as ageing tests of ballistic products and raw-materials dedicated for ballistic goods [3 - 9]. One of the materials most widely applied for the manufacture of ballistic personal arm ours is ultra-high molecular weight polyethylene (UHMWPE) composite sheets. Analysis of the literature suggests that the degree of change induced by ageing in the polyethylene plastic was evaluated on the basis of research on the mechanical and ballistic properties of these materials as well as changes in their microstructure [10 - 12].

As is apparent from the mechanism of the thermally initiated process of polyolefin degradation with oxygen originating from the air involved, an important part of the change in the breakdown of the polymer chains is oxidation inducing the formation of carbonyl groups of acid and/or ketone, ester and peracid type [13]. The ageing processes in polyethylene and other plastics are considered by many researchers in terms of the structure of the polymer at the super-molecular level, and they mainly assess the effect of ageing processes on the degree of crystallinity [14, 15]. The spaces between the spherulites, belonging to the crystalline phase, occupy amorphous areas characterised by a disordered arrangement of macromolecules. Macromolecules in the amorphous phase act as molecules binding the crystalline areas together. The more binding molecules in the polymer, the greater its mechanical strength and resistance to degradation, because a large number of disordered polymer chains need to be destroyed in order to disturb the structure of the polymer significantly. Therefore the process of degradation occursmore rapidly in materials

Table 1. *Parameters of Dyneema® SB21 [18 – 21]. * - Each sample had a working width of 50 ± 0.5 mm and gauge length 200 ± 1 mm.*

Parameter	Measure unit	Value	Test method
Width	cm	130.0 ±0.2	PN-EN ISO 2286-1:2000
Surface mass	g/m^2	145.0± 5	PN-EN ISO 2286-2:1999
Thickness	mm	0.19 ±0.02	PN-EN ISO 2286-3:2000
Tensile strength: - longitudinal direction - transverse direction	N	6 000 ± 500 5 500 ± 500	PN-EN ISO 1421:2001
Elongation at break: - longitudinal direction - transverse direction	%	4.0 ± 0.5 3.5 ± 0.5	PN-EN ISO 1421:2001

Table 2. *Parameters of ageing of ballistic inserts subjected to the action of real and simulated ageing (mechanical load, temperature cyclic variations and testing the imitation of human sweat). „+” – sample exposed to action of ageing agent; *) – tests executed with use of fatigue tester for inserts of bullet-proof vests;**) – tests carried out in climatic chamber - KBF 240 (BINDER GmbH/Germany).*

Item	Sample	Number of accelerated ageing cycles	Simulated conditions of use				
			Simulation based on mechanical deformation*)			Human sweat simulation - exposure time, min	Thermal simulation shock**), °C
			Cycle time, s	Testing angle, °	Cycle number, pcs		
Simulated conditions of ageing – mechanical load							
1	SB21M1	0.5	4	90	825	-	-
2	SB21M2	1			1650		
3	SB21M3	2			3300		
4	SB21M4	3			4950		
5	SB21M5	4			6600		
6	SB21M6	5			8250		
7	SB21M8	6			9900		
8	SB21M9	7			11550		
Simulated conditions of ageing – mechanical load, temperature cyclic variations							
9	SB21M1(2)	0.5	4	90	825	-	+
10	SB21M2(2)	1			1650		
11	SB21M3(2)	2			3300		
12	SB21M4(2)	3			4950		
13	SB21M5(2)	4			6600		
14	SB21M6(2)	5			8250		
15	SB21M8(2)	6			9900		
16	SB21M9(2)	7			11550		
17	SB21M7(2)	3.5			5775		
Simulated conditions of ageing – mechanical load, temperature cyclic variations and action of solution imitating artificial human sweat (alkaline or acid)							
18	SB21MPT1	1	4	90	1650	30	+
19	SB21MPT2	2			3300	60	
20	SB21MPT3	3			4950	90	
21	SB21MPT4	4			6600	120	
22	SB21MPT5	5			8250	150	
23	SB21MPT6	6			9900	180	
24	SB21MPT7	7			11550	210	
Real conditions of use							
Item	Sample	Ageing in real conditions, years					
1	SB21	-					
2	SB21(07)	5					
3	SB21(05)	7					
4	SB21(03)	9					
5	SB21(99)	13					

with less disordered molecules (binding ones), where even breaking a small number of these molecules causes significant deterioration of the tensile strength [14]. Degradation processes occurring in the amorphous regions cause the breakage of the polymer chains, which can indirectly contribute to an increase in their order, that is, increasing the crystallinity degree of the sample [15]. Numerous studies have shown that the degradation process occurs faster in polymeric material with a crystallinity level greater than in samples characterised by a higher share of amorphous regions [14, 16]. Some research works have been conducted on the effects of the aging process (in real and accelerated time) on the performance and usage safety of bullet- and fragment-proof vests that would allow the determination of a curve of durability for Dyneema® SB21 material applied for the manufacture of ballistic vest inserts, as well as the time after following the deterioration of the mechanical and ballistic properties of this material [17].

The aim of the study was to develop a validated method of predicting the durability of soft ballistic inserts made of a high-strength composite based on polyethylene ultra-high molecular weight (UHMWPE) fibres.

Materials

Composite „soft” ballistic inserts made of fibres with UHMWPE (Dyneema® SB21 /DSM High Performance Fibres BV/The Netherland) were used in the study. The specification of Dyneema® SB21 is presented in ***Table 1***.

Within the scope of the present work, ballistic protection packages were prepared consisting of 22 layers of the subject product, with dimensions of 30 × 36 cm. They were placed in a cover made of additional fabric.

Tests of accelerated ageing were executed on ballistic protective inserts made of a Dyneema® SB21 sheet .The subject of the study was also Dyneema® SB21 based ballistic inserts, collected after 5, 7, 9 and 13 years, used in real condition. Before testing, the ballistic inserts were subjected to visual inspection.

Methods

Research programme for the prediction of ballistic product durability

According to the risk analysis and feedback received from the end-user of bullet- and fragment-proof vests, taking into account the ways of using them in real conditions, assumptions were made for the research within this scope. The research assumptions included simulation of the use of bullet- and fragment-proof vests. Changes in the properties of ballistic body armour have several underlying causes. The basic ones are listed here:

- mechanical fatigue occurring due to deformations of the inserts, friction between the ballistic plate and outside layer of fabric, deformations which occur due to transport and storage conditions;
- fatigue caused by foreign objects inside the ballistic insert, such as dust and water;
- fatigue caused by the penetration of the ballistic insert by salt and moisture from perspiration.

Taking the above-mentioned reasons into account, a program for the examination of the use of soft ballistic inserts was created. Simulation of the normal use of a composite soft ballistic insert in enhanced aging conditions required us to choose proper parameters of the simulated environment, which were to be as real as possible (***Table 2***).

The research program took following three procedures of the aging simulation of the ballistic inserts into account:
- procedure 1 – applying a mechanical load to the insert;
- procedure 2 – applying a mechanical load along with a temperature cycle to the insert;
- procedure 3 – applying a mechanical load, temperature cycle and liquid solution simulating human perspiration to the insert.

The procedures were verified experimentally by examining the inserts made out of soft composite polyethylene Dyneema® SB 21. Also verification by means of Snedecor's F-test was carried out [22]. The analysis made it possible to determine the differences in the intensity of the impact of simulation factors used in the different procedures on the composite soft ballistic insert.

Mechanical load simulation

The wear resulting from mechanical deformations (cyclic local deformations resulting from the design and action of the wearing agent) of the ballistic inserts was simulated on a testing stand designed for the fatigue-test (Lodz University of Technology, Department of Strength of Materials, Poland), as shown in the ***Figure 1***.

Programming the measurement system consisted of entering the following parameters into the control system:
- cycle number within the range of 1 - 100,000,000;
- single cycle time within the range of 1 - 60 s;
- testing angle within the range of 10° up to 90° (every 10°).

The fatigue research program included a number of stress cycles that reflected the real time of use. It was assumed that the ballistic vest was used 52 weeks a year, including:
- 3 days a week (during 1 h of training);
- 2 days a week (6 h of field use).

According to the assumption above, the mechanical fatigue cycle of the Dyneema® SB21 composite was characterised by the number of deformation cycles that took place on the fatigue examination station.

The number of cycles on the station, taking into consideration a 1-year period (N), was described with ***Equation 1***:

$$N = n \times k \qquad (1)$$

N – number of deformation cycles that took part on the fatigue examination station in relation to the one year cycle,
n – number of days the vest is used during a year – 33 days,
k – number of deformations per day – 50.

The number of deformation cycles on the station in relation to 'x' number of years of using the vest was calculated with the use of the following ***Equation 2***:

$$N = n \times k \times x \qquad (2)$$

x – simulated time of use (1 - 7 years).

Simulation of the penetration of artificial human sweat into the ballistic insert

Simulation of the penetration of artificial human perspiration into the ballistic insert was carried out in accordance with the PN-EN ISO 105-E04:2011 standard [23].

The simulation process of using the composite 'soft' ballistic inserts consisted of the immersion of the test object for a specific time in the following solutions:
- alkaline (pH 8), with the following contents of 1 dm^3: 0.5 g L-histidine hydrochloride ($C_6H_9O_2N_3 \cdot HCl \cdot H_2O$), (0.05%); 5 g sodium chloride (NaCl), (0.5%); 2.5 g disodium hydrogen ortohophosphatedihydrate ($Na_2HPO_4 \cdot 2H_2O$), (0.25%) filled to 1 dm^3 by distilled water;
- acid (pH 5.5), with the following contents of 1 dm^3: 0.5 g L-histidine hydrochloride ($C_6H_9O_2N_3 \cdot HCl \cdot H_2O$) (0.05%); 5 g sodium chloride (NaCl) (0.5%); 2.2 g sodium dihydrogen orthophosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) (0.22%) filled to 1 dm^3 by distilled water.

The use simulation included the immersion of the whole ballistic insert in a solution simulating human sweat, where the test solution was a mixture of acid and alkaline sweat solutions at a ratio of 1:1. The test procedure consisted of the total immersion of the whole ballistic insert for a defined time (30, 60, 90, 120, 150, 180 and 210 minutes, respectively) in the test solution at room temperature followed by four-hours of incubation at a

Figure 1. *Test stand for fatigue-test of inserts for bullet-proof vests.*

temperature of 37 ± 2 °C in an oven under an load of 2,000 kg/m^2.

Thermal shock simulation

Simulation of fatigue resulting from cyclic temperature changes was carried out in accordance with NO-06-A107:2005 norm methodology [24].

Samples were exposed to the action of three temperature cycles, each of which held the sample at a temperature of:

- -40 ± 2 °C for 2 h;
- +50 ± 2 °C for 2 h.

The test was carried out in a KBF 240 climatic chamber (BINDER GmbH/Germany).

Analytical methods

Mechanical properties

Tensile strength measurements of samples before and after ageing were conducted according to the PN-EN ISO 1421:2001 standard [21] using the mechanical testing system Zwick, type Roell Z050 (Zwick/Germany), allowing the determination of tensile strength up to 50 kN.

Ballistic properties

The tests of accelerated ballistic insert ageing were conducted according to the requirements of testing methodology included in the NATO STANAG 2920:1996 Sandard [25].

The weight of the Dyneema® SB21 ballistic inserts were designated before testing and were subjected to thermal conditioning at a temperature of 20 ± 3 °C and air relative humidity of 65 ± 5% for not less than 12 hours. After shooting the necessary number of shots, the V_{50}1) parameter was calculated as the arithmetic mean of the three highest determined impact velocities causing non-perforation and of the three lowest recorded impact velocities causing perforation, provided the difference between those velocities did not exceed the value of 40 m/s. The tests of the natural ageing ballistic insert were performed according to the requirements and methods included in the PN-V-87000:1999 standard [26].

Lead core pistol bullets 7.62 × 25 mm TT with an impact velocity of 420^{+15} m/s were used for the bullet-proofness tests.

During the tests the following parameters were determined:

a) impact velocity of bullet V_{up} in m/s,
b) depth of test base deformation U_d in mm,
c) number of punctured layers.

FTIR-ATR

The progress of ageing of the Dyneema® SB21 ballistic inserts was evaluated on the basis of structural changes analysed by infrared spectroscopy within wave numbers of 400 - 4000 cm^{-1}. The tests were conducted with a Nicolet 6700 FTIR–spectrophotometer (Integrating Sphere Near-IR) from THERMO Scientific (USA).

The starting point for the test with the ATR technique was cutting the samples to 20 × 20 mm and imposing them onto the crystal, clamping them properly. In order to execute the test, the measurement was performed twice: the background spectrum, i.e. the crystal alone and the spectrum of the crystal with the sample. A background measure recording in the internal memory of the spectrophotometer was automatically subtracted upon measurement of a sample, which eliminates the environmental impact on test results.

Differential scanning calorimetry (DSC)

Thermal analysis in an inert atmosphere (nitrogen) was performed with the use of a Differential Scanning Calorimeter from Mettler Toledo (Switzerland).

A sample of 8 - 10 mg was placed in a thermal analyser furnace and heated at a rate of 10 °C/min up to a temperature of 180 °C. The sample was maintained at this temperature for 5 minutes and then cooled to a temperature of -60 °C at a rate of 10 °C/min., and then heated again to 180 °C at a rate of 10 °C/min. On the basis of DSC curves the phase transition temperatures of the test material were determined.

With the DSC method the crystallinity index (x_c) of the samples tested was calculated according to ***Equation 3*** [27]:

$$x_c = \frac{\Delta h_m}{\Delta h_m^0} \times 100\% \qquad (3)$$

where: x_c - crystallinity index; Δh_m - fusion heat of polymer sample; Δh^0_m - fusion heat of 100% crystalline polymer – for polyethylene $\Delta h^0_m = 293$ J/g.

Statistical analysis

In order to verify the relevance of differences between the sets of results of the Dyneema® SB21 test, which was carried out in three aging-simulating procedures, ANOVA was implemented and the Snedecor-F distribution test applied. Additionally the procedures were validated, which was applied for selected time periods of the mechanical strength examination for a doubled number of tests. The variation equality of these tests was then tested with the Snedecor-F distribution test. The F parameter was determined through calculation of the standard deviation (S_1) for the first series of n results (x_i) for $f_1 = n - 1$ degrees of freedom in accordance with ***Equation 4***, as well as the standard deviation (S_2) for the second series of m (y_i) for $f_2 = m - 1$ degrees of freedom, in accordance with ***Equation 5***.

$$F = \frac{S_1^2}{S_2^2} \quad S_1^2 \geq S_2^2 \qquad (4)$$

$$F = \frac{S_1^2}{S_2^2} \quad S_2^2 \geq S_1^2 \qquad (5)$$

Assuming the confidence level is 0.95 and by using statistical tables, the critical value of Fα was determined. In all cases, F < Fα, and this allows us to claim that the methods compared do not differ within the scope of precision. Additionally the results of the research became the subject of statistical analysis, namely the t-Student distribution 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, specifically those exceeding the scope of the intervals, were rejected. A hypothesis was also formed regarding the equality of the average results achieved for the selected time-periods with a double number of tests. The t_{obl} statistic value was calculated in accordance with the following equation:

$$t_{obl} = \frac{|x_1 - x_2|}{\sqrt{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}} \sqrt{\frac{n_1 n_2 (n_1 + n_2 - 2)}{n_1 + n_2}} \qquad (6)$$

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

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

S_1^2, S_2^2 – variances achieved 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 that in the t-Student factor tables, thus the difference between the results was related solely to accidental errors. Hence the validation procedures were as good as the reference ones [22].

Results and discussion

Mechanical properties

Within the scope of the research the mechanical properties of Dyneema® SB21 from new ballistic packages were examined. The tests simulated normal use (laboratory aging) in accordance with the research program determined. Additionally packages that had been used normally, in a natural manner, for 5, 7, 9 and 13 years were also tested. The differences between the three procedures of simulation of the aging of the ballistic insert were verified by:

- Procedure 1 – effects of the mechanical load,
- Procedure 2 – effects of the mechanical load and temperature cycle,
- Procedure 3 – effects of the mechanical load, temperature cycle and solution simulating human perspiration

We used the Snedecor-F test [22], making it possible to compare variances between the first and second fatigue procedure simulated, as well as between the second and third procedure in normal conditions. With the following data at our disposal:

n_z – the number of first procedure tests (population 1)

n_k – the number of second procedure tests (population 2)

The following calculations were made: S_1^2 and S_2^2 - variances of populations 1 and 2, numbering the variances in such a way that:

$$S_1^2 > S_2^2$$

$$n_z = n_1 \text{ and } n_k = n_2 \text{ or } n_z = n_2 \text{ and } n_k = n_1$$

Later the F statistical value was calculated according to the following formula (7):

$$F = \frac{S_1^2}{S_2^2} = 1.100 \qquad (7)$$

Assuming the statistical significance was $\alpha = 0.05$ and by using the statistical tables, a critical value of $F\alpha = 4.284$ was found for k_1 and k_2 degrees of freedom, related to the number of tests, respectively n_1 and n_2. $F < F\alpha$ is proof that there is no difference between variances 1 and 2 of the simulated fatigue, which means that

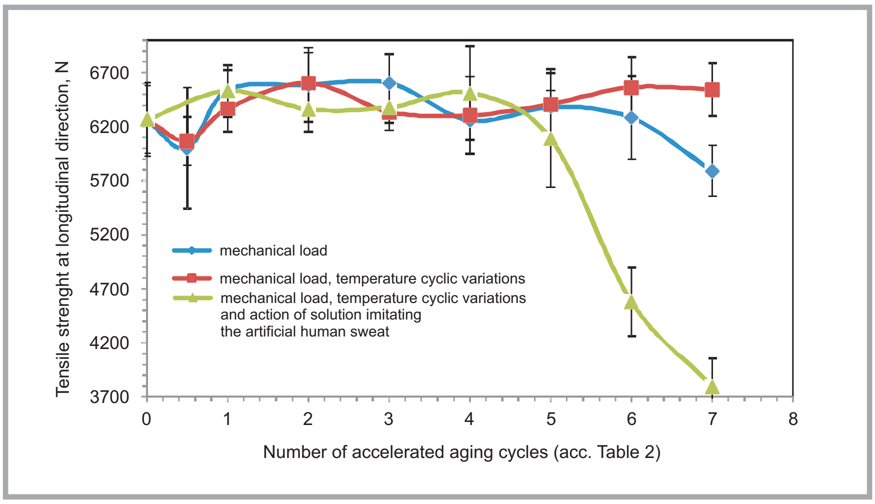

Figure 2. *Dependence of the breaking load (longitudinal direction) on the number of years Dyneema® SB 21 exposed to a mechanical load, temperature cycle and human perspiration solution is used.*

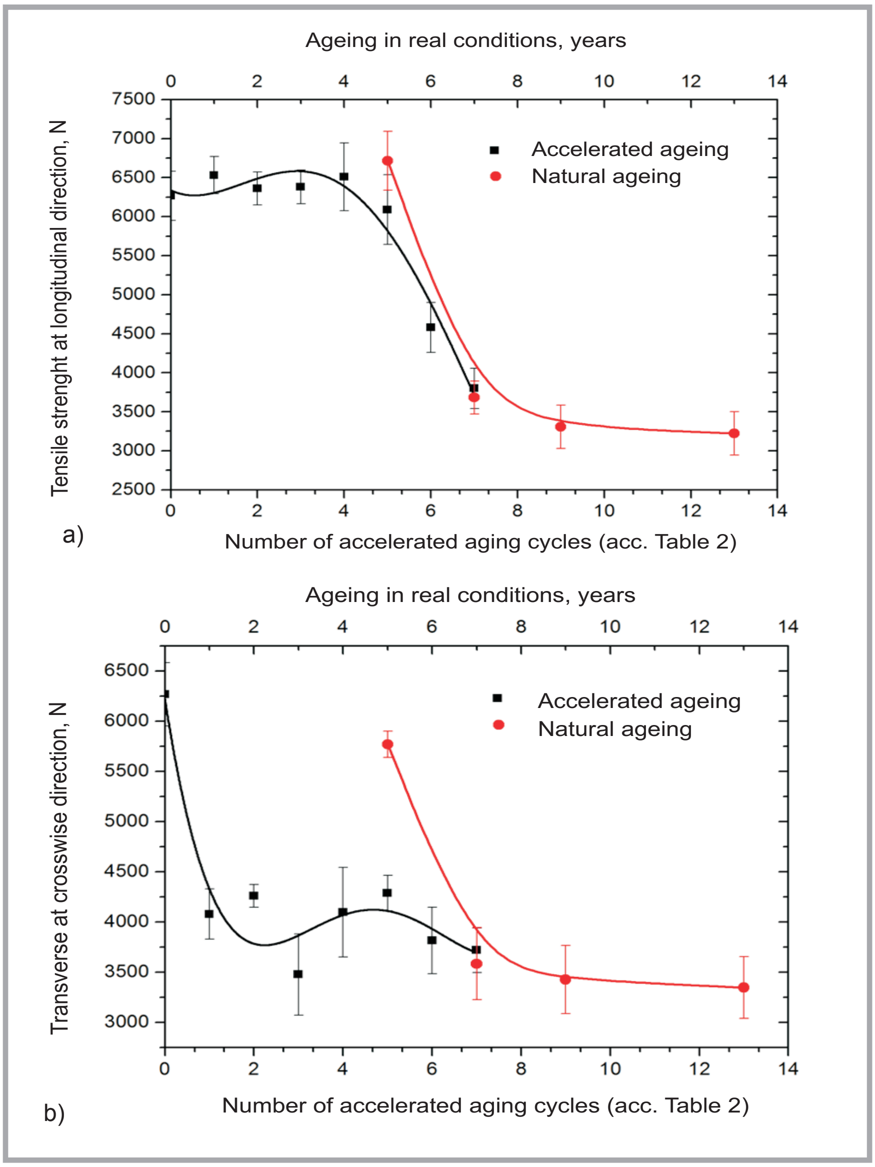

Figure 3. *Effect of the number of years of normal use of Dyneema®SB21 inserts, and of that exposed to the effect of a mechanical load, cyclic temperature variations and solution simulating human sweat on the tensile strength in the longitudinal (a) and transverse (b) direction.*

***Table 3.** Elongation at maximum force of Dyneema® SB21 inserts after real time use and accelerated ageing.*

Sample	Elongation at maximum force, %	
	longitudinal direction	transverse direction
SB21(07)	4.7 ± 0.5	4.6 ± 0.5
SB21(05)	4.0 ± 0.5	4.1 ± 0.5
SB21(03)	3.9 ± 0.5	4.6 ± 0.5
SB21(99)	4.1 ± 0.5	4.5 ± 0.5
SB21MPT1	4.1 ± 0.5	3.7 ± 0.5
SB21MPT2	4.3 ± 0.5	3.7 ± 0.5
SB21MPT3	3.9 ± 0.5	3.8 ± 0.5
SB21MPT4	4.0 ± 0.5	3.9 ± 0.5
SB21MPT5	4.2 ± 0.5	3.8 ± 0.5
SB21MPT6	4.1 ± 0.5	4.1 ± 0.5
SB21MPT7	4.3 ± 0.5	4.3 ± 0.5

the fatigue factors assumed in both cases have the same impact on the Dyneema® SB 21 composite. On the other hand, the analysis carried out for procedures 2 and 3 of the simulated fatigue proved with the $F > F\alpha$, result that there are significant statistical differences between the fatigue procedures applied in the case of the Dyneema® SB21 composite. There was a variable, depending on the fatigue procedure applied, impact of the simulation on the mechanical strength of the composite examined. The basic experimental data, presented in ***Figure 2***, shows that the co-effect of the mechanical load, temperature cycle as well as the solution simulating human perspiration (samples from SB21MPT1 to SB21MPT2), worsens significantly the strength properties of the Dyneema® SB21 composite, which cannot be observed when this composite is not subjected to the fatigue factors used in procedures 1 and 2. Taking into account the results of the above research and using the 3rd procedure of simulated aging, a method for determining the lifespan of the composite was created. This method assumed, in accordance with the goal of the experiment, a permissible change within the property examined. Then critical values of the fatigue factors that would cause that change were established. Mechanical properties of the Dyneema® SB21 composite examined in this way made it possible to establish a lifespan curve for this material. These properties also allowed the researchers to determine the critical numbers of fatigue cycles, the temperature cycles and time of exposure to the solution simulating human perspiration, after which a change in the property examined by a defined value would be noted. Thus during the course of the research the composite examined was under the influence of all three fatigue factors simultaneously (mechanical load, temperature cycle and a solution simulating human perspiration).

Research on the mechanical strength of the Dyneema® SB21 exposed to the effect of all factors was able to determine the tensile strength corresponding to that of the composite of the Dyneema® SB21 collected from the inserts of ballistic vests after 5, 7, 9, 13 years of regular usage. Analysis of the charts shown in ***Figures 3*** and ***4*** indicates that the mechanical properties – tensile strength (in the longitudinal or transverse direction) of the Dyneema® SB21 after 5 years of real-time use do not change in comparison to the value for the initial Dyneema® SB21. A rapid decrease in the tensile strength of the subject comes after 5 years of ageing under real conditions of use, as well as after 5 years under simulated ageing, which corresponds to the effect of 8250 fatigue cycles, cyclic variations of temperature and 150 min. of immersion in solution simulating human sweat.

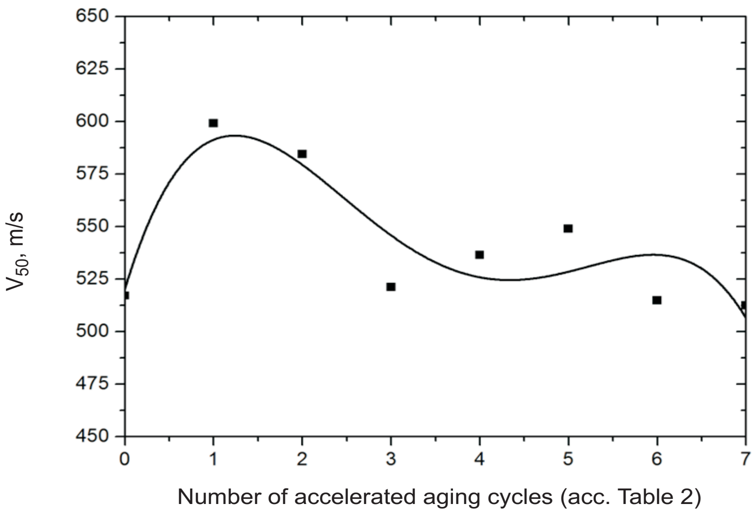

***Figure 5.** Effect of simulated ageing of Dyneema® SB21ballistic inserts exposed to the impact of a mechanical load, cyclic variations of temperature and solution which simulates human sweat on V50 detected.*

The studies helped to identify the relationship between mechanical parameters (breaking strength) of the products subjected to the standard operation (ageing in real time), and the mechanical parameters of the model in the process of undergoing accelerated time. Values of relative elongation at a maximum force were varied for all test samples, ranging from 3.9 to 4.7%, irrespective of the intensification of the ageing factors applied, as presented in ***Table 3***.

Ballistic properties

The ballistic tests executed indicate that the action of mechanical loads, cyclic temperature variations (-40 °C, +50 °C) and an additional ageing factor, being artificial human sweat, as shown in ***Figure 5***, on the material tested causes an improvement in ballistic properties (V_{50}) at the initial stage of the ageing process. However, in the course of further accelerated ageing a decrease in V_{50} occurs. The above-mentioned phenomenon of the composite tested might be a result of the overlapping of the effects of various ageing processes, such as cracking chains (leading to a decrease in V_{50}), or the creation of branches and cross-linking (increase in V_{50}) [10 - 12].

On the basis of results of the research done according to the PN-V-87000:1999 standard, it was proven that the 3rd class of naturally aged ballistic insert protecting against a 7.62 × 25 mm TT lead core, 5.5 g pistol bullets at a impact velocity of 420^{+15} m/s maintains the protective properties declared.

The research results show an increase in punctured layers of the ballistic insert as a function of natural time aging at an average of 10% for each period of natural ageing (after 5, 7, 9 and 13 years) compared to unused ballistic inserts.

FTIR spectra

Within the ATR-FTIR spectra of all samples of Dyneema® SB21 tested, the absorption bands were observed at similar ranges of wavenumbers. In the FTIR spectra, absorption bands corresponding to atom vibrations of the (CH$_2$) groups were present (at λ = 2920 cm^{-1}, λ=2858 cm^{-1}, λ=1473 cm^{-1} λ=1380 cm^{-1}, λ=719 cm^{-1} & λ=730 cm^{-1}) [28]. Moreover in the FTIR spectra of the Dyneema® SB21 absorption bands appear which correspond to atom vibrations of (C=C) groups in the wave number range of λ = 1640 - 1660 cm^{-1}. The presence of these bands might be explained by the composition of the Dyneema® SB21 composite, which is as follows:

- 73% fibres (high molecular weight polyethylene, UHMWPE);
- 10% foil-matrix (low density polyethylene);
- 17% binder (a chloroform-soluble residue - polyisoprene) [17].

During degradation resulting from the continuous action of an ageing agent (for example, temperature, humidity, mechanical deformations) more radicals appear than for samples from ballistic inserts used in real conditions. Furthermore changes in the chemical compositions are stronger in the samples exposed to accelerated ageing compared to materials aged in a natural way [10, 11]. During the process of thermally initiated degradation and progressing with the oxygen atmosphere involved, an important factor of changing the polymer chains' structure is oxidising them, which creates carbonyl groups of acid, ketone, ester and superacid type [17, 28, 29]. Analysis of ATR-FTIR spectra, as shown in ***Figure 6***, of Dyneema® SB21 samples exposed to a mechanical load, cyclic temperature variations and artificial sweat allowed to observe the increase in the intensity of (C-CH$_3$) groups (δsym C-H) within the wave number range of λ = 1380 cm^{-1} (samples SB21 MPT1- SB21 MPT7). Additionally an increase in the band intensity was observed within the range of λ = 1355 - 1385 cm^{-1}, which arises from appearing in ester groups C-O-C, (CO-CH$_3$,O-CO-CH$_3$) [28, 29]. The result proves that the accelerated ageing process causes the breakage of molecular chains, which leads to a change in the structure of the macromolecules and, consequently, to a decrease in molecular weight and deterioration of the mechanical properties of the polymer.

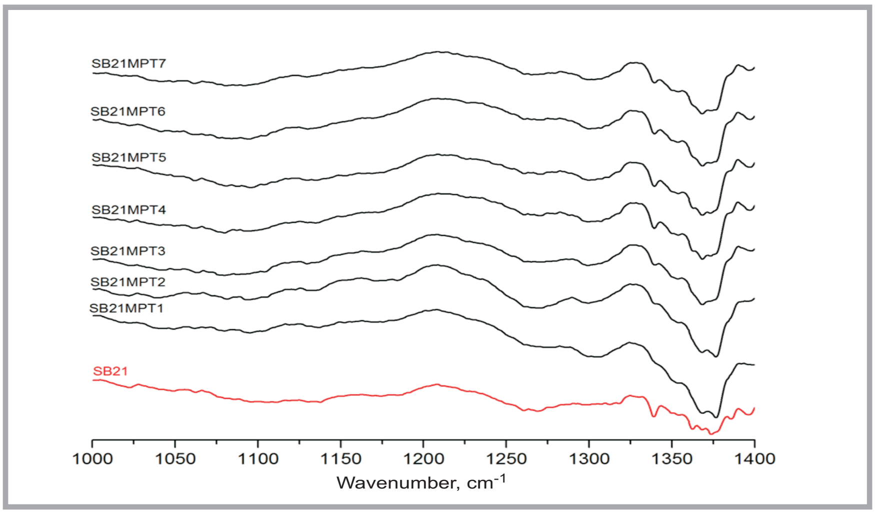

Figure 6. *ATR-FTIR spectral analysis in the range of the absorption bands resulting from groups formed during the progress of Dyneema® SB21 degradation when the sample was exposed to a mechanical load, cyclic temperature variations and artificial human sweat.*

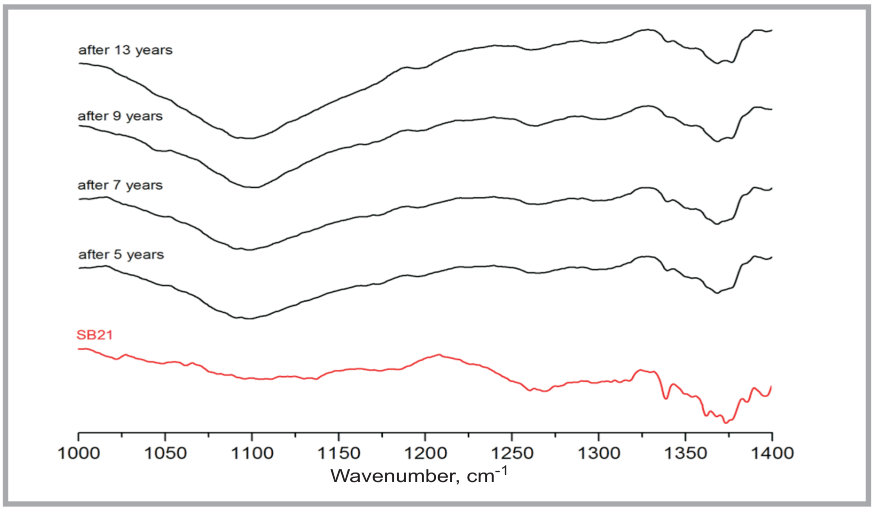

Figure 7. *ATR-FTIR spectral analysis in the range of the absorption bands resulting from groups formed during the progress of ageing in real conditions of use of Dyneema® SB21 ballistic inserts.*

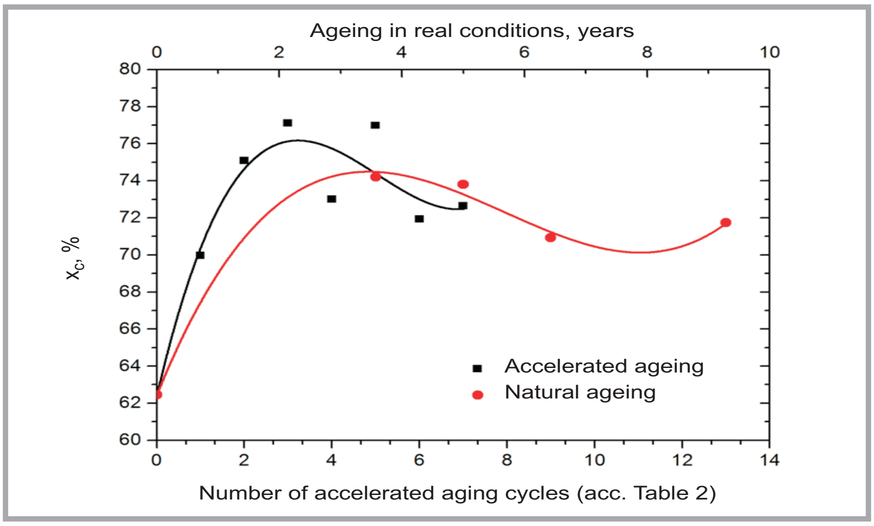

Figure 8. *Effect of the time of simulated usage of Dyneema® SB21, subjected to a mechanical load, cyclic temperature changes and solution simulating sweat on its crystallinity index (measurement of the crystallinity rate was made for one sample at a given time of simulation).*

Table 4. DSC analysis results of Dyneema® SB21. 1) melting point of 'corrugated lamellas' 135 - 139 °C, 2) melting point of rhombic crystals 147 - 151 °C, 3) melting point of pseudo-hexagonal mesophase 152 - 155 °C, 4) melting point of mono crystals 157 °C, 5) melting point of low-molecular polyethylene 123 - 126 °C.

Samples	1st heating							2nd heating			
	T_m, °C					ΔH, J/g	x_C, %	T_m, °C		ΔH, J/g	x_C, %
	4	3	2	2	5			1	5		
SB21	157.0	153.4	-	-	126.0	183.4	62.4	139.6	-	146.6	50.0
SB21 (07)	-	152.3	150.8	147.8	123.1	217.3	74.2	136.3	123.5	149.4	50.3
SB21(05)	-	152.1	150.8	147.7	123.3	216.3	73.8	136.5	123.5	149.4	51.0
SB21(03)	-	-	151.6	-	123.4	207.8	70.9	136.6	124.3	142.2	48.5
SB21(99)	-	-	151.0	147.9	121.8	210.2	71.7	136.6	110.1	143.9	49.1
SB21MPT1	-	153.9	150.8	-	123.6	206.0	70.0	135.8	125.0	133.7	45.6
SB21MPT2	-	-	150.3	148.1	123.3	220.1	75.1	135.5	125.0	138.0	47.1
SB21MPT3	-	153.9	-	149.0	123.3	225.9	77.1	135.8	125.4	143.7	49.0
SB21MPT4	-	153.4	151.5	148.2	123.2	213.9	73.0	136.0	125.6	135.8	46.3
SB21MPT5	-	153.2	150.4	149.0	123.4	225.6	77.0	135.9	124.3	144.4	49.3
SB21MPT6	-	-	150.6	-	123.6	210.8	71.9	135.7	124.8	133.7	45.6
SB21MPT7	-	152.8	150.7	149.2	123.5	212.9	72.6	135.7	125.0	138.4	47.2

Spectra of samples of the Dyneema ® SB21 composite used under natural conditions were also analysed, showing a significant increase in band intensities within the range of λ = 1050 - 1125 cm^{-1} originating from ester groups type C-O-C [25, 26], which was not observed in the spectra of Dyneema® SB21 samples exposed to accelerated ageing, as shown in the ***Figure 7***.

Differential scanning calorimetry (DSC)

The progress of ageing was evaluated on the basis of the thermal properties of samples tested before and after ageing, both under accelerated and real conditions. Results of the DSC analysis are listed in ***Table 4***. The course of the DSC graphs as well as the in-depth analysis of thermal effects of the material tested showed that the content of crystalline phase with a melting point above 157 °C is characteristic only for Dyneema® SB21 not subjected to the effect of accelerated or natural ageing. Dyneema® SB21 under real as well as accelerated ageing has crystalline phase containing various crystalline structures. During the first heating, DSC endothermic peaks of the test samples subjected to ageing are assigned to the melting of the following crystalline structures [17]:

1. rhombic crystals – melting point (147 - 151 °C);
2. pseudo-hexagonal mesophase – melting point (152 - 155 °C);
3. mono-crystals – melting point (157 °C).

In the course of the DSC research, during the second heating, an endothermic peak was observed originating from the melting of corrugated lamellas at a temperature of about 135 - 137 °C, while no peaks originating from crystalline forms which appear during the first heating were observed. It can be assumed that during the second constant heating of the samples tested a process of unifying the crystalline structure of polyolefin of Dyneema® SB21 occurred. Moreover a peak originating from the crystalline structure of a melting point of 123 - 126 °C appears on the DSC curves during both the first and second heating. Based on literature [14 - 17] one can assume that the peak's presence on the DSC curve is related to the presence of low-molecular crystalline phase, which is a compound of Dyneema® SB21. From the perspective of the research completed a change is noticeable in the character of the crystalline phase of aged samples, compared to Dyneema® SB21 not subjected to the effect of laboratory ageing. The crystallinity index of the samples tested is presented in ***Table 4***.

The experimental data show that the range of ageing processes in the samples tested affects the change in x_c remarkably. The crystallinity index of Dyneema® SB21 aged under real or accelerated conditions has a value of 70% to 77%, whereas x_c determined after the second heating has a value ranging from 45% to 55%. One may assume that the difference between the first Dyneema® SB21 x_c achieved during the first and second heating is determined by the effects of time and temperature on the material tested. Having analysed the results of the research gathered, we may state that the ageing processes occurring both under real and accelerated conditions affect significantly the value of x_c of the material tested. A remarkable increase in $x_c$occurs in samples of Dyneema® SB21 exposed to accelerated ageing, as shown in ***Figure 8***.

Literature [14 - 17] indicate that the above phenomenon is probably connected with the degradation processes occurring in the amorphous regions and causing the breakage of chains, which may indirectly contribute to an increase in their order, i.e. increasing the sample's crystallinity. When analysing the results of the research we also observe a decrease in the x_c of Dyneema® SB21 subjected to the effect of accelerated ageing, which is induced by the phenomena of branching and cross-linking reactions in the material tested, which compete with chains breaking.

Summary and conclusions

The main goal of the research work was to develop a research programme for simulation of using soft ballistic inserts. The programme of research elaborated for simulation of using soft ballistic inserts was done by the execution of tests on Dyneema® SB21 material according to the programme developed.

The research has proven that there is a wide impact of the procedures of use on the mechanical properties of the Dyneema® SB21 composite. The results obtained in the analysis of variance F-Snedecor test allowed the rejection of the null hypothesis due to the lack of differences in the effects on the properties of the Dyneema® SB 21 composite's simulated aging procedures. The experimental data presented prove that the co-effect of the mechanical load, temperature cycle and an additional factor – a solution simulating human perspiration (samples SB21MPT1 – SB21MPT2) has a detrimental effect on the strength properties of the Dyneema® SB21 composite examined. This was not observable in the case of the 1st and 2nd fatigue procedures. The experimental data presented indicate that the results of action of the ageing agents (mechanical load, temperature cyclic variations and artificial human sweat) on the Dyneema® SB21 material, strengthen each other, and the behaviour of the material is resultant of all these effects. The impact of the ageing agents causes a significant deterioration in mechanical and ballistic properties of Dyneema® SB21, progressive over exposure time. It is triggered by alteration of the chemical structure of macromolecules, which finds confirmation in the presence of absorption bands originating from C-O-C groups in the FTIR spectra of the composite tested, as well as from changes of crystallinity over the time of ageing. Calculation of the tensile force corresponding to the breaking force of the Dyneema® SB21 collected from the inserts of ballistic vests after 5, 7, 9 & 13 years of usage under natural conditions was possible thanks to the analysis of mechanical properties of the Dyneema® SB21 composite subjected to the action of all ageing agents applied in the experiment. The analysis of data indicates that the mechanical properties – value of the tensile strength of Dyneema® SB21 after 5 years of real-time usage shows no change compared to the value of the above parameter of new Dyneema® SB21. A rapid decrease in the tensile strength value occurs after 5 years of natural ageing and after 5 years of simulated ageing, which corresponds to an effect of 8250 fatigue cycles, cyclic temperatures and 150 min. of immersion in solution simulating human sweat. Moreover the properties of Dyneema® SB21 tested allowed for the drafting of a curve of the material strength course, as well as to determine the critical ageing time, after which a change in the property tested by a particular value occurs. Analysis of mechanical and ballistic properties of Dyneema® SB21 allowed the determination of the correlation between the parameters of products undergoing the standard operation (ageing in real time), with the model processes running in accelerated time.

Editorial note

1) Ballistic Limit: For a given bullet type, the velocity at which the bullet is expected to perforate the armor 50% of the time. The ballistic limit is typically denoted as the V_{50} or V_{50} value - according to NATO STANAG 2920:1996 Standard.

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