Marzena Fejdyś*,
Marcin Łandwijt,
Agnieszka Kucharska-Jastrząbek,
Marcin H. Struszczyk

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

The Effect of Processing Conditions on the Performance of UHMWPE-Fibre Reinforced Polymer Matrix Composites

DOI: 10.5604/12303666.1201140

Abstract
The aim of this study was to analyse the influence of the main pressing parameter, i.e. temperature of a ultra-high molecular weight polyethylene (UHMWPE) fibrous sheet Dyneema® HB26, on the performance of resultant UHMWPE-fibre reinforced polymer matrix composites intended for the manufacturing of ballistic personal protection. The main goal of this research was to connect the pressing temperature of the initial polyethylene fibrous material and the main performance feature, i.e. the ballistic behaviour of the resultant composites. The polyethylene composites, designed at various temperatures, were subjected to testing of ballistic, mechanical, thermal (DSC) and structural (FTIR) properties, as well as the surface topography by means of scanning electron microscopy (SEM). Attempts were made to determine the correlation between ballistic and mechanical properties of the various types of polyethylene composites designed and their structural and surface properties. Phenomena accompanying the pressing process of the fibrous polyethylene composites at various temperatures are discussed along with attempts to estimate the mechanisms of changes. This research allowed for the determination of optimal pressing conditions for fibrous polyethylene material to obtain a composite with optimal features for ballistic and personal protection application.

Key words: *ballistic armour, personal protection, ultra-high molecular weight polyethylene (UHMWPE), fibrous polyethylene composites, design process.*

Introduction

One of the materials most widely applied in the manufacturing of ballistic personal armours is ultra-high molecular weight polyethylene (UHMWPE) in a fibrous form. The application of UHMWPE fibres in the manufacturing of ballistic personal protection is due to their properties, e.g., high mechanical strength, abrasion resistance, a low friction coefficient, resistance to water, aggressive chemicals and UV radiation [1-5]. Due to the very high velocity of sound propagation of UHMWPE fibres, they may absorb large amounts of energy, which, in accordance with the above-mentioned properties, determines their suitability for ballistic applications. The behaviour of UHMWPE fibres is directly dependent on their chemical composition and crystalline structure [2, 3]. The high degree of UHMWPE crystallinity (up to 85%) results from the oriented polymer structure (over 95%), which is formed by macromolecular chains in parallel arrangement [2]. The weak van der Waals bonds between polyolefin chains affect the low temperature resistance. Under the influence of local temperature, crystalline areas transform into amorphous ones. The UHMWPE melting point is 144 - 152 °C, which allows the use of fibres at a temperature not exceeding 100 °C for a long period [4].

UHMWPE fibres are used both in typical woven structures and in fibrous materials, developed specially for ballistic purposes [5 - 11]. UHMWPE fibres are typically combined with low molecular weight thermoplastic polymers to form unidirectional several-ply-thick fibres. These plies are then stacked in a $[0/90]_2$ sequence to create 4-ply thick tapes that can be warm-consolidated (just below the melting point of crystalline polymer fibre) to form laminated materials with fibre volume fractions by approximately 85%.

UHMWPE-fibre reinforced polymer matrix composites exhibit remarkable resistance to penetration during localised impact loading by blunt projectiles [12 - 19]. The performance is dependent on the composite architecture as well as on the fibre and (to lesser extent) matrix properties. However, there is growing experimental evidence that the matrix shear strength (governing the inter-laminar shear strength) has a significant influence on the ballistic performance of UHMWPE composites [12, 17, 20 - 22]. Furthermore Greenhalgh et al. [23] reported a detailed fractographic study and argued qualitatively that the matrix shear strength influences the energy absorption and failure mechanisms, such as delamination and splitting. Fibrous ballistic materials made of UHMWPE fibres in the form of multi-ply stitched packets create so-called soft ballistic armours (e.g., body armours, anti-fragmentation covers), and in the form of pressed polymer matrix composites, they create rigid ballistic armours (e.g., protective helmets, shields, armours). The manufacturing of hard protective inserts is based on the process of thermal and pressure combinations of fibrous UHMWPE sheets. The pressing process of the polyethylene product includes several stages [12, 24].

Cut ply precursors are piled up, with the number of sheets depending on the protection level desired. Then they are placed into a hot hydraulic press which transforms them into a hard plate, and the glue from the original film manufacturing helps to bond the layers together in the heat of the process [24]. The plies are pressed together at a temperature of 127 °C and consolidation pressure of 20.6 MPa for 20 min to produce a laminate [12]. Epoxy or polyurethane is usually used as a matrix (glue) in the UHMWPE-fibre reinforced plate [12, 24 - 26].

Although UHMWPE composite manufacturing technology is well known, there are a limited number of scientific publications on the influence of the pressing pro-

cess temperature on the thermal, structural, mechanical and ballistic properties of polyethylene products. There are also no reports on changes in the properties of the polyethylene composite depending on the pressing temperature.

The studies prepared indicated that the appropriate processing parameters of the UHMWPE-fibre reinforced polymer matrix composite design may be attributed to the possibility that their performance is a function of the structural properties designed.

The research also attempts to explain the processes occurring in composites pressed at various temperatures. The thesis of this study is that there is a range of optimal pressing temperatures for the properties of the UHMWPE-fibre reinforced polymer matrix composites produced intended for the manufacturing of ballistic personal armours.

■ **Research subject**

Dyneema®HB26 (DSM High Performance Fibres BV, The Netherlands) made of UHMWPE fibres was used for the manufacturing of UHMWPE-fibre reinforced polymer matrix composites. The main properties of Dyneema® HB26 are presented in *Table 1*.

■ **Methods**

Pressing

The UHMWPE-fibre reinforced polymer matrix composites (i.e., the multi-ply polyethylene plates) were manufactured by pressing 45 plies of Dyneema®HB26 using a PHM 250E press (Ponar Żywiec, Poland). The pressing process includes three stages (see *Figure 1*).

Various pressing temperatures were chosen, as shown in *Table 2*. The pressing temperature of the UHMWPE-fibre reinforced polymer matrix composites was determined using the press sensor (T_{press}) and sensors, i.e., 3 thermocouples, which were located between the Dyneema®HB26 sheets during the pressing process (T_{packet}). The measurement uncertainty of the temperature was determined in both cases at a level of ± 1 °C.

As a result of the pressing process of the polyethylene sheets within a temperature range (T_{press}) from 115°C to 160°C, profiles of 3D UHMWPE-fibre reinforced

polymer matrix composites with dimensions of 25×30 cm and surface mass of 12.0 ± 0.1 kg/m² were obtained. However, as a result of the increasing temperature of the pressing process up to $T_{press} = 175$ °C, the polyethylene composite was permanently deformed. Examples of the UHMWPE composites pressed at temperatures from $T_{press} = 115$ °C to $T_{press} = 175$ °C are presented in *Figure 2*.

Analytical methods

Evaluation of Dyneema®HB26 mechanical properties

Tests of the mechanical properties of the Dyneema®HB26 were performed according to the following standards: PN-EN ISO 2286-1:2000 [27], PN-EN ISO 2286-2:1999 [28], PN-EN ISO 2286-3:2000 [29], PN-EN ISO 1421:2001 [30], and PN-EN ISO 4674-1:2005 [31], the results of which are presented in *Table 1*.

Table 1. *Properties of the nonwoven polyethylene product Dyneema®HB26 used in the study.*

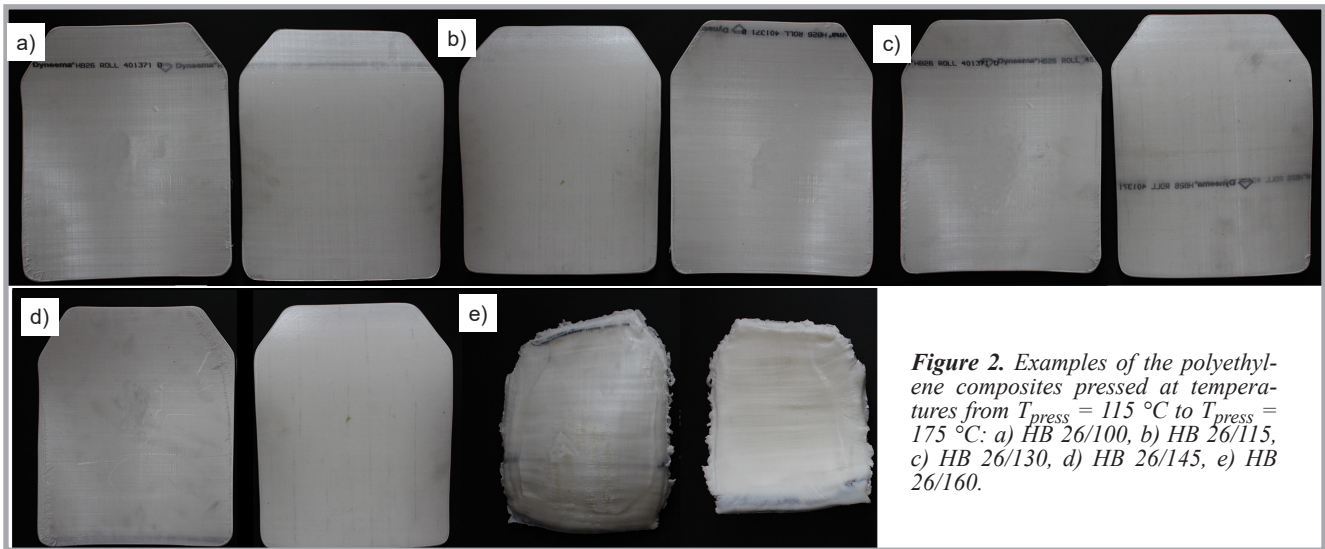| Parameter	Unit	Value	Testing procedure
Width	cm	160.0 ± 0.1	PN-EN ISO 2286-1:2000 [27]
Areal density	g/m²	262 ± 1	PN-EN ISO 2286-2:1999 [28]
Thickness	mm	0.36 ± 0.01	PN-EN ISO 2286-3:2000 [29]
Breaking force: lengthwise crosswise	kN	9.37 ± 0.24 8.48 ± 0.21	PN-EN ISO 1421/1:2001 [30]
Elongation at break: lengthwise crosswise	%	3.6 ± 0.1 3.2 ± 0.1	PN-EN ISO 1421/1:2001 [30]
Tear resistance: lengthwise crosswise	N	no tearing	PN-EN ISO 4674-1:2005 [31]

Figure 1. *Parameters of the pressing process of the UHMWPE-fibre reinforced polymer matrix composites.*

Table 2. *Parameters of the pressing process of the UHMWPE-fibre reinforced polymer matrix composites.*

Sample symbol	T_{press}, °C	T_{packet}, °C
HB 26/100	115	100
HB 26/115	130	115
HB 26/130	145	130
HB 26/145	160	145
HB 26/160	175	160

Figure 2. *Examples of the polyethylene composites pressed at temperatures from $T_{press} = 115\ °C$ to $T_{press} = 175\ °C$: a) HB 26/100, b) HB 26/115, c) HB 26/130, d) HB 26/145, e) HB 26/160.*

Tests of ballistic resistance and hardness of polyethylene composites

A cycle of ballistic tests of the UHMWPE-fibre reinforced polymer matrix composites manufactured was conducted according to procedure PBB-31:2014 [32] based on Standard PN-V-87000:2011 [33]. The test was accomplished with 7.62×25 TT FMJS munitions, with a mass of 5.5 ± 0.1 g, at various predefined speeds of the projectile impact, i.e., within $V_m = 400 - 700$ m/s.

This range was selected as a result of the initial tests on the assumption that the projectile cannot shoot completely through the object tested. As in the case of the ballistic tests on the testing base, the depth of deformation of the base (H_{dp}) was measured exactly to 0.1 mm after every shot. The results of sample tests of the composites received shot with 7.62 mm TT FMJS munitions were statistically interpreted. A reference
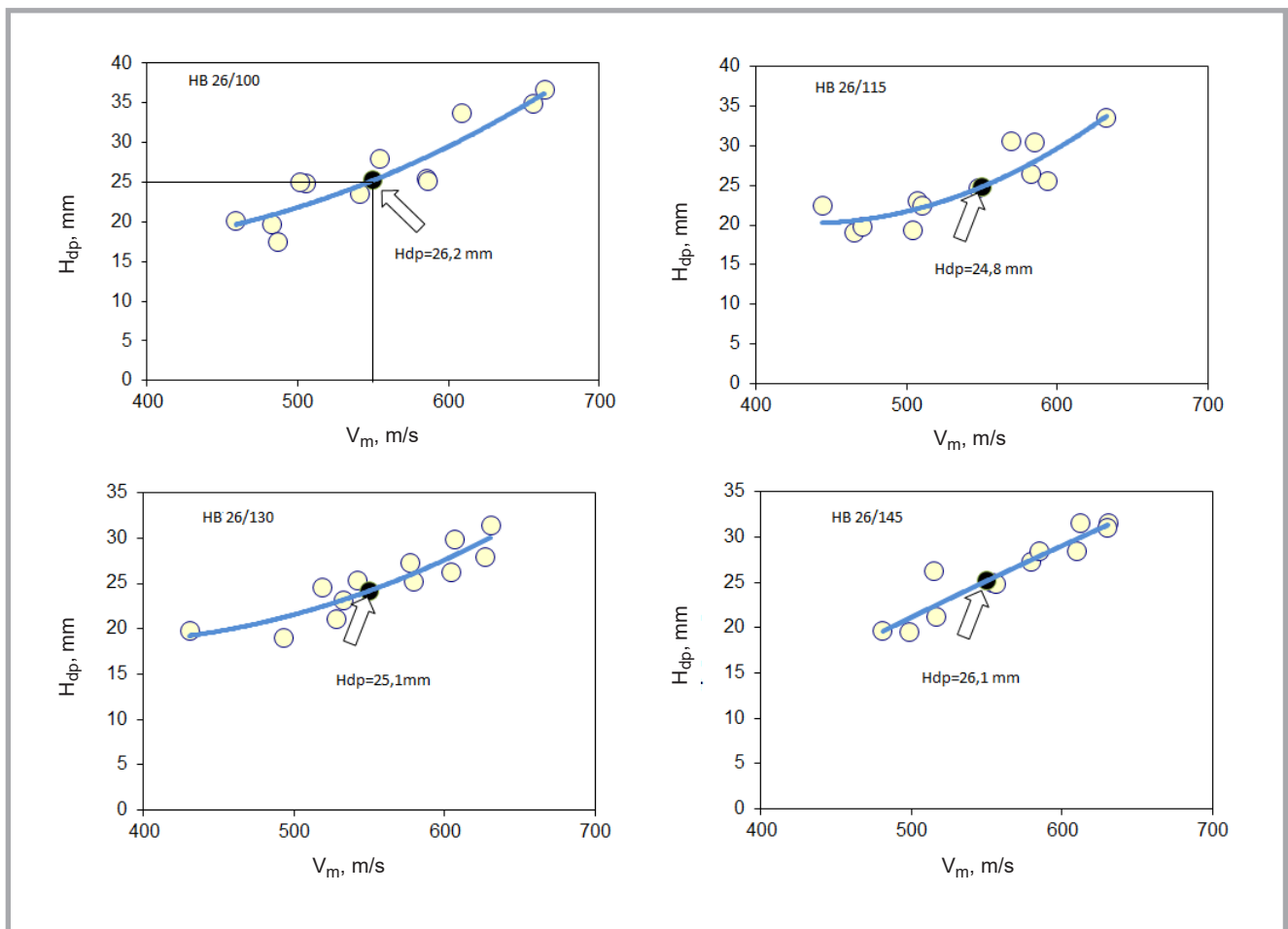
Figure 3. *Determination of the deformation of the base H_{dp} of the polyethylene composites at a selected reference speed of a 7.62 mm TT FMJS projectile equal to $V_m = 550$ m/s.*

speed of V_m = 550 m/s was selected for the 7.62 mm TT FMJS projectile, being of a medium a range of 400 - 700 m/s, at which gunfire was carried out.

Hardness tests were performed according to PN-EN ISO 2039-2 [34], by determination of the hardness of plastics when pressing using a Rockwell hardness tester (KBPruftechnik, Germany) and Rockwell M hardness scale (main load of 980.7 N, ball diameter of 6.35 mm).

FTIR
FTIR tests of the Dyneema®HB26 and the UHMWPE-fibre reinforced polymer matrix composites were conducted by means of an FTIR spectrophotometer - NICOLET iS10 (Thermo Scientific, USA) by the method of multiple attenuated total reflectance (ATR) within a wavelength range from 400 to 4000 cm^{-1}.

Thermal analysis (DSC)
Thermal analysis of the Dyneema®HB26 and the UHMWPE-fibre reinforced polymer matrix composites was conducted using inert gas (nitrogen) and a differential scanning calorimeter - DSC1 from Mettler Toledo (USA), calibrated based on reference standards: ind and n-octane.

The following measurement program was used:
■ heating from -80 °C to 200 °C (heating speed 10 °C/min);
■ cooling from 200 °C to -80 °C (heating speed 10 °C/min);
■ second heating from -80 °C to 200 °C (heating speed 10 °C/min).

On the basis of the DSC thermograms achieved, the temperature range and heating effect (enthalpy) of the crystallisation and melting processes of the crystalline phase were determined. The crystallisation degree of the UHMWPE-fibre reinforced polymer matrix composites was calculated according to the following formula:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \text{ in \%} \quad [1]$$

where, 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 (ΔH_m^0 = 293 J/g) [35].

SEM analysis
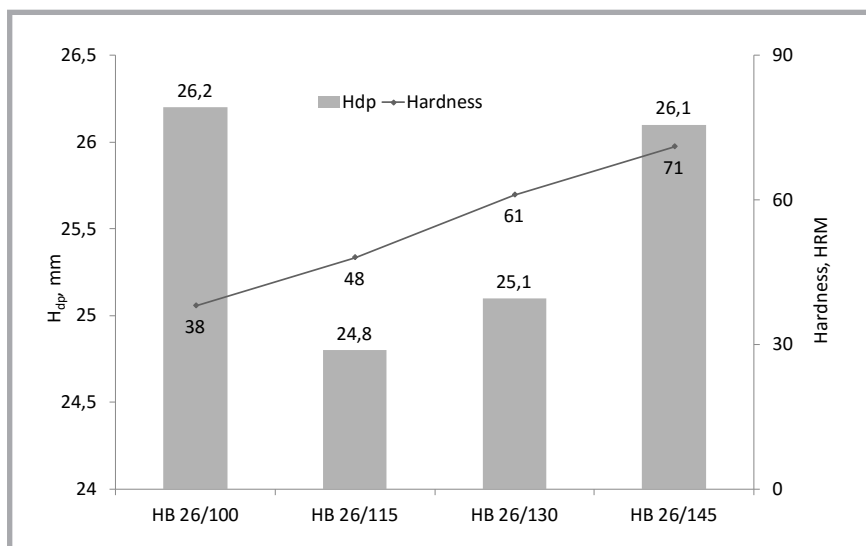SEM analysis was performed under low vacuum conditions (40 Pa) by means of a Quanta 650F microscope (FEI, USA), in the backscattered electron (BSE) mode. The surface image was recorded at a magnification of 2263×.

Analysis of results
Evaluation of the ballistic resistance and hardness of the polyethylene composites
The results received of sample tests of the UHMWPE-fibre reinforced polymer matrix composites shot with 7.62 mm TT FMJS munitions were statistically interpreted. *Figure 3* presents graphs of $H_{dp} = f(V_m)$, on the basis of which the deformation of the base H_{dp} of the UHMWPE-fibre reinforced polymer matrix composites was determined for a selected reference speed of 7.62 mm TT FMJS projectile equal to V_m = 550 m/s.

The ballistic tests showed that the pressing temperature significantly affects the ballistic resistance of the UHMWPE-fibre reinforced polymer matrix composites, expressed by the deformation of the base H_{dp}, which is presented in *Figures 3 & 4*.

The highest values of deformation of the base were noted in the case of UHMWPE-fibre reinforced polymer matrix composites of HB 26/100 and HB 26/145, amounting to H_{dp} = 26.2 mm and H_{dp} = 26.1 mm, respectively. In the case of sample HB 26/100, the deformation of the base likely resulted from the fact that in this case the pressing temperature is significantly lower than the recommended temperature [12, 24], limiting chemical reactions (poly-addition) in the Dyneema®HB26 binder, and thereby reducing the bonding quality of the Dyneema®HB26 plies.

It can be assumed that this is the main reason for the weakening of ballistic properties of the HB 26/100 composite. However, in the case of HB 26/145, the increase in deformation of the base and the reduction in ballistic resistance likely resulted from the reactions of the degradation occurring at a pressing temperature of 145 °C, causing polymer chain breaking, branching and cross-linking. Due to the deformation of the HB 26/160 composite pressed at a temperature of 175 °C, its ballistic properties and hardness were not evaluated.

The lowest value of deformation of the base was noted for the HB 26/115 composite, amounting to H_{dp} = 24.8 mm. This composite was pressed at a temperature of 130 °C.

Analysis of the hardness of the UHMWPE-fibre reinforced polymer matrix composites tested determined by the Rockwell method in the M scale showed that the hardness of the samples tested increased with increasing pressing temperature (*Figure 4*).

An increase in the pressing temperature affects the growth of hardness of the composite by 10 units on average every 15°C. The explanation of this phenomenon, as in the case of ballistic resistance, can be found in the degradation and cross-linking processes, which coexist and occur in the pressed Dyneema®HB26 polyethylene material. Thus the changes

Figure 4. Dependence of H_{dp} and hardness of the polyethylene composites and the pressing temperature of Dyneema® HB26.
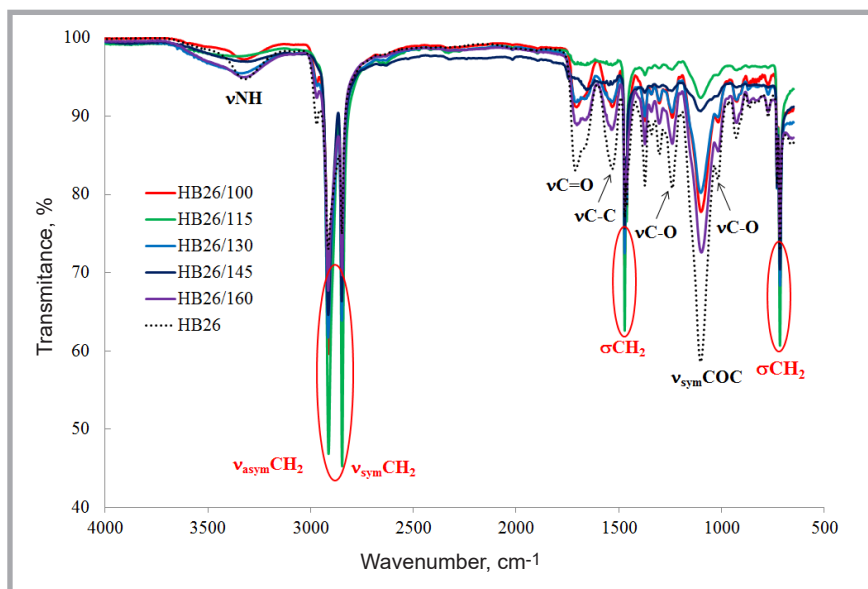
Figure 5. *ATR-FTIR spectra of UHMWPE-fibre reinforced polymer matrix composites pressed at various temperatures.*

Table 3. *Specific absorption bands of Dyneema® HB26.*

Wave number, cm⁻¹		Group or bonding	Kind of vibration
Marked	**Literature data [37, 38]**		
3300	3380-3420	OC(=O)NH OH	ν
2970	2950-2975	CH₃	ν
2910	2915-2940	CH₂	ν
2845	2840-2870	CH₂	ν
1700	1650-1690	C=O	ν
1528	1510-1530	C-C C=N=O OC(=O)NH	ν
1470	1440-1465	CH₂	ν
1370	1370-1390	CH₂	δ
1335	1315-1340	O-CH₃	δ
1305	1285-1350	CH₂ OC(=O)NH	δ
1245	1185-1275	C=N=O OC(=O)NH	ν
1072	1050-1160	C-O-C	ν
1015	1000-1100	C-O-C	ν
927	800-950	CH₂	δ
716	720-725	CH₂	(-CH₂-)ₙ>₄

in the Dyneema®HB26 product lead to the formation of free radicals, which is primarily manifested by the degradation and decrease in the molecular mass of the polymer, as well as by its cross-linking, which is, in turn, reflected by the increase in molecular mass. It can be assumed that the ongoing cross-linking process is connected with the formation of three-dimensional networks in the surface ply, which produces features of non-fusible and insoluble gelling to the material, thereby improving the material hardness [36].

Considering that ballistic tests and hardness analysis were conducted to confirm the considerations above, structural studies were conducted to evaluate the surfaces of the UHMWPE-fibre reinforced polymer matrix composites. Attempts were made to determine the correlation between ballistic and mechanical properties and structural and surface behaviour.

ATR-FTIR analysis
The ATR-FTIR data received from the analysis of the Dyneema®HB26 are presented as numerical data. Only some of the most characteristic signals were selected from the experimental data for two essential reasons: This study is not focused on the technical side of spectra analysis, but rather the use of the spectrum analysed

for identification of the binder composition of the Dyneema®HB26. There were absorption bands present in the ATR-FTIR spectrum of Dyneema®HB26, corresponding to the vibrations of grouping atoms, as shown in ***Table 3***.

The nature of the ATR-FTIR spectrum of the Dyneema®HB26 tested indicates the presence of groupings typical of polyethylene molecules [39]. Additionally there are intensive bands typical of polyurethanes and ether compounds within a wave range of 1072 cm⁻¹ (ν sym. C-O-C), 1015 cm⁻¹ (ν asym. C-O-C), 1700 cm⁻¹ (ν C=O), 1528 cm⁻¹ (δ NH, C=N), 1305 cm⁻¹ (ν C=N, NH), and 1245 cm⁻¹ (ν C=N, NH).

In the course of the aforementioned analysis, it can be concluded that the binder of Dyneema®HB26 constitutes a polymer composition on the basis of polyether diols, isocyanates as well as polyurethanes. The composition of the binder identified is confirmed in the literature [40, 41]. Data on the chemical structure of the binder allowed for determination of the probable processes which occur when Dyneema®HB26 is pressed at various temperatures.

In the ATR-FTIR spectra of polyethylene composites made of Dyneema®HB26 pressed at various temperatures, as presented in ***Figure 5,*** absorption bands were recorded within the range of the same wavelengths, as in the case of the non-pressed Dyneema®HB26.

However, comparing the bands in the polyethylene composites, it can be noticed that depending on the pressing temperature of the Dyneema®HB26 used, they differ significantly in terms of signal intensities originating from the same chemical groupings. In particular, this phenomenon is visible in the case of samples of the HB26/100 and HB 26/160 polyethylene composites, pressed at temperatures of 115 °C or 160 °C, respectively. In these two cases, significant changes occur in the intensities of the bands originating from the following groupings:

■ CH₂ (2910 cm⁻¹, 2845 cm⁻¹, 1470 cm⁻¹, 1370 cm⁻¹, 927 cm⁻¹, 716 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);

in relation to these band intensities, the HB 26/115, HB 26/130 andHB 26/145 polyethylene composites were noted.
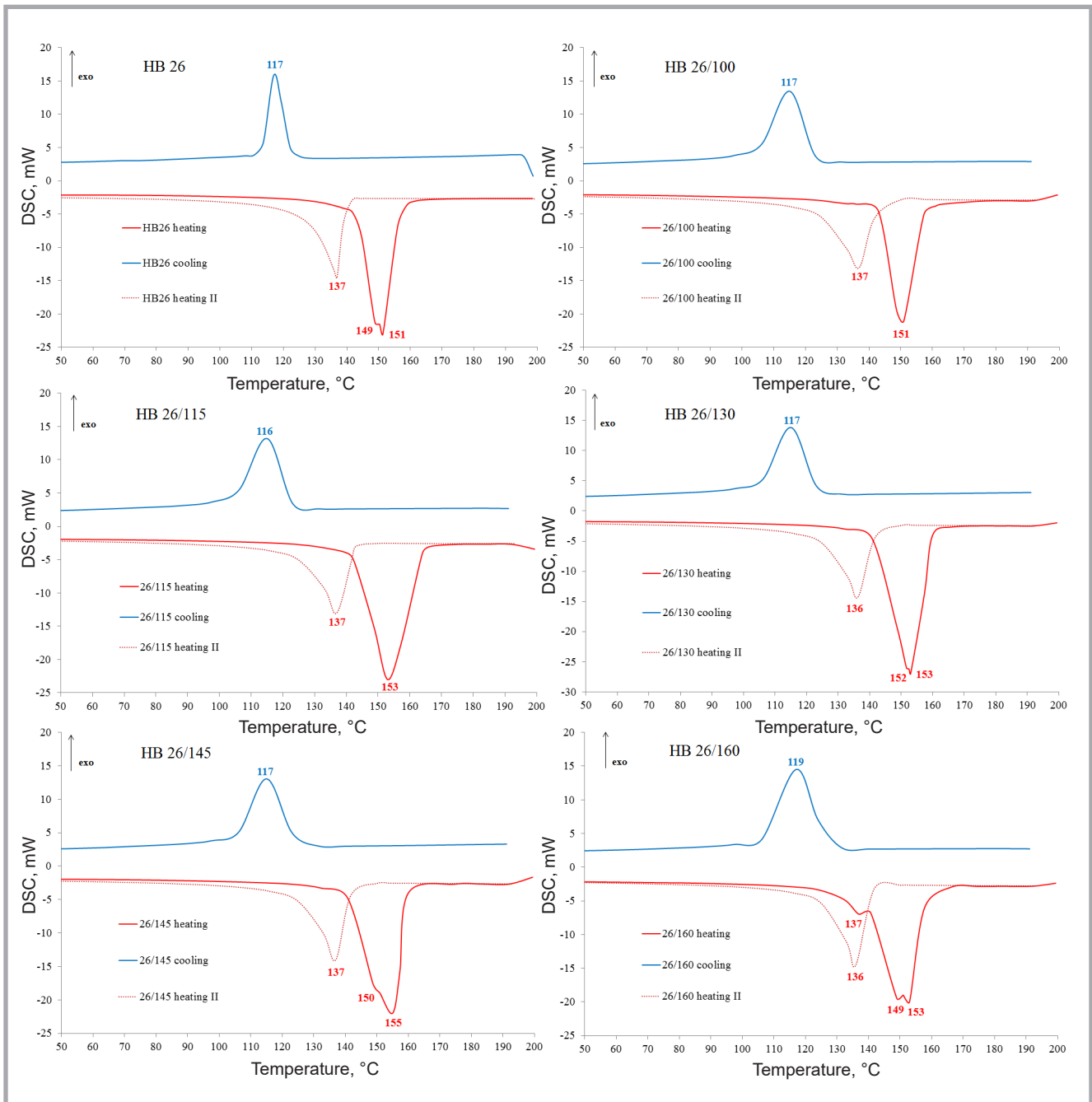
Figure 6. DSC curves of the Dyneema®HB26 and the UHMWPE-fibre reinforced polymer matrix composites fabricated at various temperatures.

Table 4. DSC analysis results of the Dyneema® HB26 and UHMWPE-fibre reinforced polymer matrix composites. T_m – melting point of crystalline phase, ΔT_m - melting point range of crystalline phase, ΔH_m - enthalpy connected with melting process of crystalline phase, T_c – temperature of crystallisation, ΔT_c – temperature range of crystallisation, ΔH_c – enthalpy connected with crystallisation process.

| Sample symbol	Heating				Cooling			Second heating			
	T_m, °C	ΔT_m, °C	ΔH_m, J/g	X_c, %	T_c, °C	ΔT_c, °C	ΔH_c, J/g	T_m, °C	ΔT_m, °C	ΔH_m, J/g	X_c, %
Dyneema® HB26	151; 149	143-161	-206	70	117	122-106	109	137	127-143	-122	42
HB 26/100	151	143-163	-203	69	117	122-106	107	137	126-143	-110	38
HB 26/115	153	144-164	-203	69	116	122-106	103	137	127-143	-107	36
HB 26/130	152; 153	142-160	-191	65	117	123-107	105	136	127-142	-104	35
HB 26/145	150; 155	142-162	-210	65	117	123-108	106	137	127-142	-111	38
HB 26/160	137; 149; 153	142-165	-167	57	119	125-111	108	136	127-141	-110	37

Considering the structure of the binder of Dyneema®HB26, it can be assumed that polyaddition reactions, based on the reaction of isocyanate groups with hydroxy groups originating from polyether diols, occurred in the binder in the pressing process of these materials, which leads to the formation of urethane groups, according to *Equation 2* (see page 118) [42]:
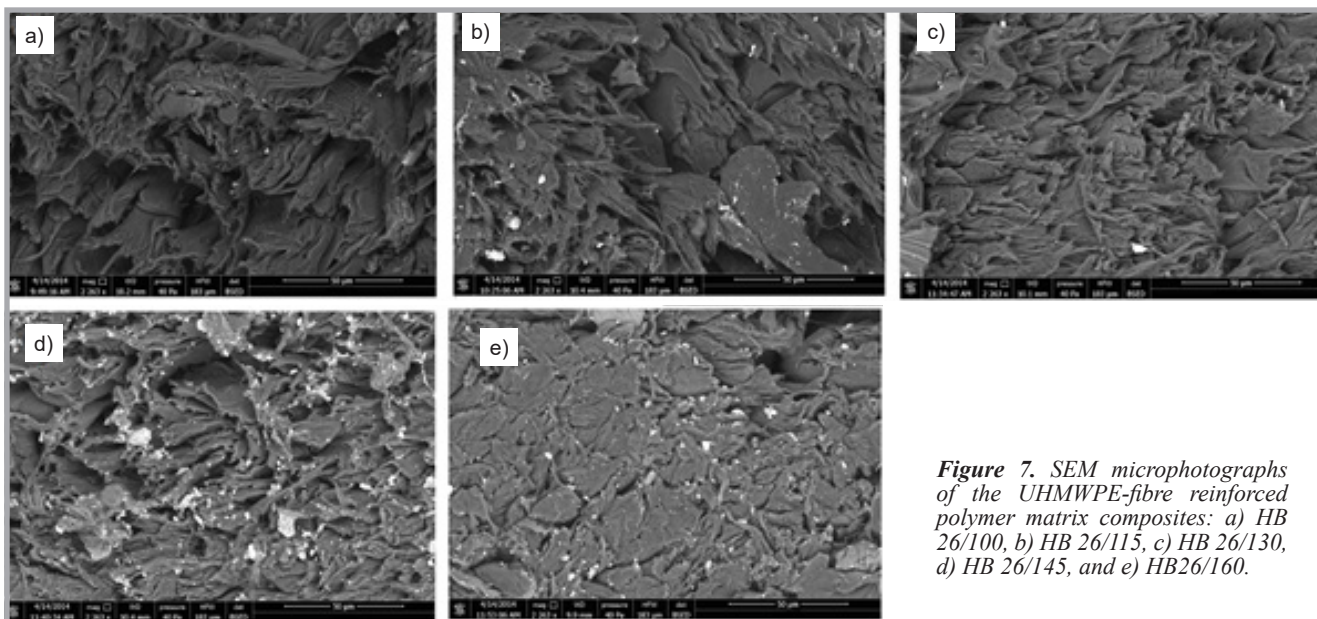
Figure 7. *SEM microphotographs of the UHMWPE-fibre reinforced polymer matrix composites: a) HB 26/100, b) HB 26/115, c) HB 26/130, d) HB 26/145, and e) HB26/160.*

$$nOCN{-}R{-}NCO + nHO{-}R'{-}OH \rightarrow$$
$$\rightarrow {-}(O{-}CONH{-}R{-}NHCO{-}O{-}R')_n{-} \quad (2)$$
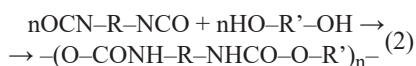
where, R, R'– residue of aliphatic hydrocarbon.

Therefore, in the HB 26/100 composite samples, in the case in which the pressing temperature was significantly lower than the recommended temperature [12, 24], reactions in the Dyneema®HB26 binder typical of polyurethanes were limited. The significant intensity of the peaks originating from polyether diols, isocyanates and polyurethanes is noticeable. In the case of the HB 26/115 composite samples, where the pressing temperature used was 130 °C, which was compliant with the recommended temperature [12, 24], typical bands of the chemical groupings, identified as groupings entering into the composition of the binder (i.e., polyether diols, isocyanates and polyurethanes), had practically disappeared.

In the case of these samples, a significant increase in the intensity of the bands originating from groupings typical of polyethylene (at $\lambda = 2910$ cm^{-1}, $\lambda = 2845$ cm^{-1}, $\lambda = 1470$ cm^{-1}, $\lambda = 1370$ cm^{-1}, $\lambda = 927$ cm^{-1} and $\lambda = 716$ cm^{-1}) was observed. However, in the HB 26/160 polyethylene composites, where the pressing temperature ($T_{press} = 175$ °C was significantly higher than the recommended temperature, the significant intensity of the peaks originating from groups NH, OH ($\lambda = 3300$ cm^{-1}), COC ($\lambda = 1072$ cm^{-1}, $\lambda = 1015$ cm^{-1}) & C=O (1735 - 1600 cm^{-1}) as well as the signals originating from groupings COC ($\lambda = 1100$ cm^{-1}) and forming ester groupings COC (COCH$_3$, OCOCH$_3$) within 1355 - 1385 cm^{-1} [40], was noticed once again.

The increase in intensity of these signals in the case of the HB 26/160 composite is probably related to the intensive processes of thermal degradation that occur when the polyethylene material is pressed at a temperature of 175 °C. The thermal degradation of UHMWPE-fibre reinforced polymer matrix composites constitutes a radical process, as a result of which hydrogen atoms are detached from the CH$_2$ groupings in the main polymer chain and macro-radicals are formed. In addition to the breaking of the main polymer chain, the presence of carbonyl groups in UHMWPE-fibre reinforced polymer matrix composites favours the breakdown of chains to free radicals initiated by the temperature as a result of the detachment of oxygen atoms. In the thermally initiated degradation process, oxidation, causing the formation of acid, ketone, ester and peracid type carbonyl groupings, is also an essential element of the changes in the structure of polymer chains [40].

The pressing process of Dyneema®HB26 performed at a higher temperature than the recommended temperature causes an increase in the reaction of degradation intensity, including breaking and crosslinking reactions, which in turn leads to structural changes in the macromolecules and properties of the materials.

Thermal analysis (DSC)
The DSC thermograms presented in ***Figure 6*** (see page 117) were performed to determine the thermal properties of the Dyneema®HB26 and the UHMWPE-fibre reinforced polymer matrix composites. The results of the DSC analysis are included in ***Table 4*** (see page 117).

On the basis of the analysis of the DSC thermograms listed (***Figure 6***) and data included in ***Table 4***, the pressing temperature of Dyneema®HB26 affected the nature of physical processes in the structure of the resultant UHMWPE-fibre reinforced polymer matrix composites.

During the first heating, theendothermic peaks of DSC curves of the samples tested are assigned to the melting of the following crystalline structures [43]:
■ folded fins - melting point of 135 - 139 °C;
■ diamond crystals - melting point of 149 - 152 °C;
■ pseudo hexagonal mesophase - melting point of 153 - 155 °C.

During the second heating, an endothermic peak originating from the melting of folded fins at a temperature of 135 - 139 °C is noticed. However, peaks originating from the other crystalline forms present during the first heating are not noticed. Thus it can be assumed that during the second heating of the samples tested at a constant speed, unification of the crystalline structure of the Dyneema®HB26 occurred. The DSC graphs as well as detailed analysis of the thermal effects of the samples tested showed that the diversity of the crystalline structures observed in the UHMWPE-fibre reinforced polymer matrix composites increased with increasing

pressing temperature. In the case of the 26/100 and 26/115 polyethylene composites pressed at temperatures of 115 °C or 130 °C, respectively, one crystalline phase is observed. In the case of the HB26/130 and HB26/145 polyethylene composites pressed at temperatures of 145 °C or 160 °C respectively, two crystalline phases are observed. However, for the HB26/160 polyethylene composite, three crystalline structures were detected. Results from the experimental data show that the pressing temperature of Dyneema®HB26 also significantly affects the degree of crystallinity (**Table 4**).

The value of the crystallinity degree of Dyneema®HB26 is 70%. For the HB26/100 and HB26/115 polyethylene composites, the value of the crystallinity degree is practically at the same level as that of Dyneema®HB26. A decrease in the crystallinity degree is observed for samples HB 26/130, HB 26/145 and HB 26/160, resulting from the degradation, which causes a breakdown of the chains, occurring in the composites pressed at such temperatures and contributing to the reduction of the crystallinity degree of the sample.

SEM analysis
The effect of the pressing temperature of Dyneema® HB26 on changes in the surface appearance of the samples of UHMWPE-fibre reinforced polymer matrix composite manufactured was evaluated by means of SEM spectroscopy. As for the samples of polyethylene composites tested, the number of defects in the form of overlapping surface changes increased with increasing pressing temperature. Examples of the surface morphology of samples are presented in *Figure 7*.

Changes in the surface degradation effects of the samples were caused by temperature changes. The surface of the samples of HB 26/100 and HB 26/145 polyethylene composites features few surface changes or small white areas. However, much larger white areas overlapped in multiple locations, forming a grid, which can be noticed on the surface of the samples of the composites manufactured at pressing temperatures of 145 °C or 160 °C.

Furthermore corrugations, cracks and significant roughness are visible on the surface of these composites. Areas as if separated by a border area or surrounded by cracks are observed locally along the line of the course of the cracks and

on the extension thereof. Microscope observations of the surface degradation of the samples tested are correlated with the strength, thermal and structural properties and ballistic resistance discussed.

■ Conclusions

The analysis of the effects of the pressing temperature of Dyneema®HB26 on the properties of the UHMWPE-fibre reinforced polymer matrix composites fabricated intended for the manufacturing of ballistic personal armours revealed the essential vulnerability of Dyneema®HB26 to the pressing temperature.

Despite the achievement of the composite structure, the samples of UHMWPE-fibre reinforced polymer matrix composite tested showed significant changes in properties depending on the pressing temperature.

The results of the tests performed contributed to the determination of the optimal pressing temperature of the initial Dyneema®HB26 for the ballistic behaviour of the UHMWPE-fibre reinforced polymer matrix composites fabricated. This temperature was determined by using a press sensor (T_{press}) and thermocouples located between the Dyneema®HB26 sheets during the pressing process (T_{packet}).

The optimal pressing temperatures of the Dyneema®HB26 were T_{press} = 130 °C and T_{packet} = 115 °C. A pressing temperature of the Dyneema®HB26 material exceeding T_{press} = 130 °C had a negative impact on the properties of the polyethylene composites, which became worse with increasing temperature. The increased pressing temperature can be treated as additional, long-lasting thermal processing that adversely affects the properties of UHMWPE-fibre reinforced polymer matrix composites. It can lead to degradation processes occurring in the composite structure, causing damage and deterioration of its ballistic properties.

The accelerated degradation of the materials discussed, caused by increased temperature is indicated by the reduced ballistic resistance and surface defects of the samples, which intensify as the temperature increases, reducing the degree of polymer crystallinity. The tests also demonstrated the adverse effect on the

properties of UHMWPE-fibre reinforced polymer matrix composites in the case of a pressing temperature of Dyneema®HB26 equal to T_{press} = 115 °C and T_{packet} = 100 °C. In this case, the major cause of degradation of the properties of UHMWPE-fibre reinforced polymer matrix composites is probably the limited dynamics of chemical reactions occurring in the Dyneema®HB26 binder, resulting from the low pressing temperature, which decreases the bonding quality of the particular Dyneema®HB26 plies, thus adversely affecting the properties of the product.

Moreover the oxidation of the polyethylene chain may affect a more dynamic reduction in the performance of the ballistic protectors during usage. Thus, it is most important to optimise the process of UHMWPE-fibre reinforced polymer matrix composite fabrication taking into the account not only the direct performance but also potential changes during t standard use resulting from structural and/or chemical alteration initiated by the fabrication process.

References

1. Van Dingenen JLJ. Gel-spun high-performance polyethylene fibres. In: Hearle JWS (ed) *High-performance fibers*. Cambridge: Woodhead Publishing Limited, 2004, pp. 69 – 80.
2. Redlich G, Fortuniak K. The way of use of waste of ballistic polyethylene products. *Tworzywa Sztuczne i Chemia* 2010; 3: 8.
3. Chin J, Petit S, Forster A, at al. Effect of artificial perspiration and cleaning chemical's on the mechanical and chemical properties of ballistic materials. *Journal of Applied Polymer Science* 2009; 113: 567-584.
4. Marissen R. Design with Ultra Strong Polyethylene Fibers. *Materials Sciences and Applications* 2011; 2: 319-330.
5. Fink JK. *Handbook of engineering and specialty thermoplastics, Volume 1: Polyolefins and Styrenics* New Jersey: John Wiley & Sons, Inc. Hoboken. Salem Massachusetts: Scrivener Publishing LLC, 2010, pp. 82-83.
6. Vlasblom MP and van Dingenen J. The manufacture, properties and applications of high strength, high modulus

polyethylene fibres. In: Bunsell A (ed) *Handbook of tensile properties of textile and technical fibres.* Cambridge: Woodhead Publishing, 2009, pp. 437-485.

7. Jacobs MJN, van Dingenen JLJ. Ballistic protection mechanisms in personal armour. *Journal of Materials Science* 2001; 36: 3137-3142.

8. Chocron S, Pintor A, Gálvez F, Roselló C, Cendón D, Sánchez-Gálvez V. Lightweight polyethylene non-woven felts for ballistic impact applications: material characterization. Composites Part B: Engineering 2008; 39: 1240-1246.

9. Ong CW, Boey CW, Hixson RS, Sinibaldi JO. Advanced layered personnel armor. *Int J Impact Eng* 2011; 38: 369-383.

10. Fejdyś M, Łandwijt M, Habaj W, Struszczyk MH. Ballistic helmet development using UHMWPE fibrous materials. *Fibres & Textiles in Eastern Europe* 2015; 23, 1(109): 89-97.

11. David NV, Gao X-L, Zheng JQ. Ballistic resistant body armor: contemporary and prospective materials and related protection mechanisms. *Appl Mech Rev* 2009; 5: 62.

12. Attwood JP, Khaderi SN, Karthikeyan K, et al. The out-of-plane compressive response of Dyneema® composites. *Journal of the Mechanics and Physics of Solids* 2014; 70: 200-226.

13. Iremonger MJ. Polyethylene composites for protection against high velocity small arms bullets. In: *Proceedings of the 18th International Symposium on Ballistics* (ed WG Reinecke), San Antonio TX: Technomic Publishing Company Inc, 1999, pp. 946–954.

14. Cunniff PM. Dimensionless parameters for optimization of textile-based body armor systems. In:. *Proceedings of the 18th International Symposium on Ballistics* (ed WG Reinecke), San Antonio TX: Technomic Publishing Company Inc, 1999, pp. 1303-10.

15. Morye SS, Hine PJ, Duckett RA, Bacon DJ, Ward IM. Modelling of the energy absorption by polymer composites upon ballistic impact. *Compos Sci Technol* 2000; 60: 2631-2642.

16. Jacobs MJN, Van Dingenen JLJ. Ballistic protection mechanisms in personal armour. *J Mater Sci* 2001; 36: 3137-3142.

17. Karthikeyan K, Russell BP, Fleck NA, Wadley HNG, Deshpande VS. The effect of shear strength on the ballistic response of laminated composite plates. *Eur J Mech A/Solids* 2013;42:35-53.

18. O'Masta MR, Deshpande VS, Wadley HNG. Mechanisms of projectile penetration in Dyneema® encapsulated aluminum structures. *Int J Impact Eng* 2014; 74: 16–35.

19. Polak J. Dyneema body armours. Techniczne Wyroby Włókiennicze 1997; 1: 5-9.

20. Vargas-Gonzalez L, Walsh SM, Wolbert J. Impact and ballistic response of hybridized thermoplastic laminates. Technical Report No. ARL-MR-0769, August 2011. Army Research Laboratory: Aberdeen Proving Ground MD.

21. Vargas-Gonzalez LR, Walsh SM, Gurganus JC. Examining the relationship between ballistic and structural properties of lightweight thermoplastic unidirectional composite laminates. Technical Report No. ARL-RP-0329, August 2011. Army Research Laboratory: Aberdeen Proving Ground MD.

22. Lee BL, Walsh TF, Won ST, Patts HM, Song JW, Mayer AH. Penetration failure mechanisms of armor-grade fiber composites under impact. *J Compos Mater* 2001; 35: 1605-1633.

23. Greenhalgh E, Bloodworth VM, Iannucci L, Pope D. Fractographic observations on Dyneema® composites under ballistic impact. *Compos Part A* 2013; 44: 51-62.

24. Russell BP, Karthikeyan K, Deshpande VS, Fleck NA. The high strain rate response of ultrahigh molecular-weight polyethylene: from fibre to laminate. *Int J Impact Eng* 2013; 60: 1-9.

25. O'Masta MR, Deshpande VS, Wadley HNG. Defect controlled transverse compressive strength of polyethylene fiber laminates. *International Journal of Solids and Structures* 2015; 52: 130–149

26. Shujia L, Jia W, Yanping W, Yimin W. Improving the ballistic performance of ultrahigh molecular weight polyethylene fiber reinforced composites using conch particles. *Materials and Design* 2010; 31: 1711-1715.

27. PN-EN ISO 2286-1:2000. Rubber- or plastics- coated fabrics – Determination of roll characteristics – Part 1: Methods for determination of length, width and net mass.

28. PN-EN ISO 2286-2:1999. Rubber- or plastics- coated fabrics – Determination of roll characteristics – Part 2: Methods for determination of total mass per unit area, mass per unit area of coating and mass per unit area of substrate.

29. PN-EN ISO 2286-3:2000. Rubber- or plastics- coated fabrics – Determination of roll characteristics – Part 3: Method for determination of thickness.

30. PN-EN ISO 1421:2001. Rubber- or plastics-coated fabrics – Determination of tensile strength and elongation at break.

31. PN-EN ISO 4674-1:2005. Rubber- or plastics-coated fabrics – Determination of tear resistance – Part 1: Constant rate of tear methods.

32. PBB-31:2014. Ballistic tests – Determination of ballistic resistance of sample set.

33. PN-V-87000:2011. Light ballistic armours – Ballistic protection vests – Requirements and tests.

34. PN-EN ISO 2039-2. Plastics – Determination of hardness – Part 2: Rockwell hardness.

35. Fejdyś M, Łandwijt M, Struszczyk MH. Effect of accelerated ageing conditions on the degradation process of dyneema® polyethylene composites. *Fibres & Textiles in Eastern Europe* 2011;19, 1(84):60-65.

36. Sungsik K, Young CN. Effect of radiation on ultra high molecular weight polyethylene (UHMWPE). In: Controlling of degradation effects in radiation processing of polymers. Vienna: IAEA, 2009, pp. 85-94.

37. Zieliński W. The spectroscopic methods and their application for the identification of organic compound. Warszawa: WNT, 2000.

38. Rocha M, Mansur A, Mansur H. Characterization and accelerated ageing of UHMWPE used in orthopedic prosthesis by peroxide. *Materials* 2009; 2: 562-576.

39. Fejdyś M, Cichecka M, Łandwijt M, Struszczyk MH. Prediction of the durability of composite soft ballistic inserts. *Fibres & Textiles in Eastern Europe* 2014; 22, 6(108): 81-89.

40. Karthikeyan K, Russell BP, Fleck NA, Wadley HNG, Deshpande VS. The effect of shear strength on the ballistic response of laminated composite plates. *European Journal of Mechanics A/Solids* 2013; 42: 35-53.

41. Attwood JP, Khaderi SN, Karthikeyan K, Fleck NA, O'Masta MR, Wadley HNG, Deshpande VS. The out-of-plane compressive response of image composites. *Journal of the Mechanics and Physics of Solids* 2014; 70: 200-226.

42. Guelcher SA, Gallagher KM, Didier JE, Klinedinst DB, Doctor JS, Goldstein AS, Wilkes GL, Beckman EJ, Hollinger JO. Synthesis of biocompatible segmented polyurethanes from aliphatic diisocyanates and diurea diol chain extenders. *Acta Biomaterialia* 2005; 1: 471–478.

43. Karacan I. Structure-property relationships in high-strength high-modulus polyethylene fibres. *Fibers & Textiles in Eastern Europe* 2005; 13: 15.