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Structural Changes in Fibrous Ballistic Materials During PACVD Modification

Abstract
The modification of specialized textiles including ballistic textiles by an effective and ecological technique is the main objective for screening the optimal way to obtain multi-functionalised products. The aim of the research was to optimise the method of Plasma Assisted Chemical Vapour Deposition (PACVD) of ballistic textile: p-aramid fabrics and fibrous materials made of ultra-high molecular weight polyethylene to produce a functionalized surface supported by the various kinds of deposited polymers. The research was carried out to screen the several processing parameters of PACVD with the presence of low-molecular mass organic compounds containing fluoro- or silane moieties to obtain a change in the surface behaviour of ballistic textiles. The process of PACVD allowed to effectively steer the behaviour of the surface properties of modified ballistic textiles, such as the amount of the deposited polymer and its form as well as chemical characterisation depending on the processing parameters.

Key words: *ballistic textiles, functionalization, plasma assisted chemical vapour deposition.*

Introduction

The main problem of ballistic materials is to maintain properties related to the safety and performance of ballistic protectors during long term use in various, sometimes changed, conditions. P-aramid fabrics, being the raw materials most often used for designing ballistic inserts for vest, are relatively sensitive to humidity and UV radiation. On the other hand, there are fibrous materials made of ultra height molecular weight polyeth-ylene (UHMWPE) fibres called Dynee-ma® or Spectra® which are susceptible to delamination and creasing, effecting the usability of the ballistic inserts during long term use.

The time-stable resistance of ballistic textile materials for conditions of storage and use of ballistic products provides an essential parameter related to the safety of the products. World reports indicate the influence of the chemical/physical on the reduction in ballistic efficiency of textile ballistic products during storage/use [1, 2].

Functionalisation in advanced material solutions for ballistics has become necessary and urgent due to the development and implementation of modern solutions, but in in the last 20 years the has not been dynamic. The functionalization of textile materials and products using plasma techniques is increasingly used in industrial practice, mainly due to the many benefits, often impossible to obtain using other techniques [3].

There is few literature reports concerning the modification of high-strength fibres for potential use in ballistics using the technique of plasma. For the most part, the studies are related to modifications of the following basic raw materials: fibres, yarns or, at least, aramid fabric, being purified from the processing aids.

Researches focused on improving the adhesion of UHMWPE fibres with resin or low-molecular polyethylene forming the destination matrix of the final ballistic material, inter alia by increasing the surface energy. This enables better and more durable blending of modified fibres with the matrix material [4 - 12]. The effect of plasma assisted chemical vapour deposition (PACVD) polymer deposition onto textile ballistic materials on the physical-mechanical behaviour was described in detail in [4, 13].

The aim of the research was to optimise PACVD modification of two types of unpurified technical textile materials: p-aramid fabric and UHMPWE fibrous materials, to directly obtain a functionalized surface with a highly reproductive deposited polymer.

The thesis of the study was to design a control of the process of PACVD polymeric matrix deposition onto various types of textile materials as well as use different kinds of low-molecular mass substrates.

Materials

Textile materials

Two types of the ballistic textiles were used during the study: woven fabric Style 363/120 (SAATI S.P.A, Italy), made of p-aramid yarn, and UHMWPE fibres con-

taining Dyneema® SB51 (DSM Dyneema BV/The Netherlands) material.

The main properties of the textile used are listed in **Table 1**.

The textile materials were selected on the basis of the analysis of availability, novelty aspects, (structure, material) and our experience in applying the above ballistic materials.

Substrates for PACVD

For surface modification of the textile materials selected, the following two chemicals were used:

- tetradecafluorohexane; $CF_3(CF_2)_4CF_3$; (TDFH), 99%, Tokyo Chemical Industry, Japan;
- hexamethyldisiloxane; (HMDSO); $C_6H_{18}OSi_2$, 98% Sigma Aldrich;

and gases (Air products): synthetic air, 99.995; nitrogen, 99.999; oxygen, 99.999; argon, 99.9992.

■ Methods

Surface modification of the textile materials by PACVD

Modification of the textile materials (the substrates) in glow discharges was performed in a commercial plasma jet - CD 400PLC ROLL CASSETTE (EUROPLASMA/Belgium).

The plasma jet is equipped with a vacuum system which allows to get a pressure as low as 133.3×10^{-3} Pa in the reactor and on the Baratron type vacuum gauge. The gases and vapours of the monomers are fed to the reactor in a manner controlled by the flow meters. The plasma is generated in the electric field RF 13,56 MHz, and the supplied power is adjustable up to 300 W. The plasma jet is equipped with a fine-tuning device as well as an applied and reflected power meter. Samples of textile materials were placed freely between two flat electrodes of dimensions 24 × 24 cm. (**Figure 1**).

In the course of the modification process the following parameters were monitored: pressure and temperature inside the reactor, the flow rate of gas and vapours of the monomer as well as the effective power of discharge.

The following process gases of oxidising nature were applied: synthetic air 100%, nitrogen 100% and oxygen 100%.

Table 1. *Characterisation of the textile materials used in the study: Style 363/120 [13] and Dyneema® SB51 [1].*

Textile material: Style 363/120						
Surface mass, g/m²	Thickness, mm	Tensile strength, N		Elongation at the maximum force, %		Bursting strength
		warp	weft	warp	weft	
PN-ISO 3801:1993	PN-EN ISO 5084:1999	PN-EN ISO 13934-1:2002				PN-EN 863:1999
212 ± 2	0.20 ± 0.02	6700 ± 200	6800 ± 500	7.0	5.1	79 ± 10
Textile material: Dyneema® SB51						
Surface mass, g/m²	Thickness, mm	Tensile strength, N		Elongation, %		Bursting strength
		longitudinal	vertical	longitudinal	vertical	
PN-EN ISO 2286-2:1999	PN-EN ISO 2286-3:2000	PN-EN ISO 1421:2001				PN-EN 863:1999
251 ± 2	0.19 ± 0.02	9047 ± 880	7850 ± 1020	4.3	4.1	182 ± 8

Table 2. *List of conditions of the synthesis and deposition of organofluorine coatings on p-aramid substrates as well as on fibrous sheets made of UHMWPE fibres.*

Type of monomer	Monomer flow rate, Pa·m³·s⁻¹ (in sccm)	Carrier gas flow rate, Pa·m³·s⁻¹ (in sccm)	Power, W	Time period of deposition, min	Sample
TDFH	0.016 (10)	-	100	3	F/10sccm/100W/3min
			200	3	F/10sccm/200W/3min
	0.032 (20)	-	100	3	F/20sccm/100W/3min
			200	1	F/20sccm/200W/1min
			200	3	F/20sccm/200W/3min
	0.064 (40)	-	100	3	F/40sccm/100W/3min
			200	1	F/40sccm/200W/1min
			200	3	F/40sccm/200W/3min
			250	5	F/40sccm/250W/5min

The plasma was excited in those process gases with various technical conditions:

- two variants of power applied to the reactor: 100 and 200 W,
- two variants of gas flow rate: 0.08 and 0.8 Pa m³ s⁻¹,
- three variants of time period of plasma operation on the substrates: 1, 5 and 15 min.

A 4-stage procedure of the process was established:

- 30 min. deaeration of the sample;
- cleaning the surface in Ar plasma;
- activation in the process gas – under an adopted variant of power, time and flow rate;
- 30 min. sample conditioning under a vacuum.

Organofluorine coatings were made in the plasma of the following monomer vapours: tetradecafluorohexane $CF_3(CF_2)_4CF_3$.

A 5-stage procedure of the process was established:

- 30 min. deaeration of the sample,
- cleaning the surface in Ar plasma,
- activation in the process gas,
- deposition of polymer coating,

- 30 min. sample conditioning under a vacuum after the process.

The plasma was excited in the monomer vapours with various technical conditions:

- two variants of power applied to the reactor: 100 and 200 W,
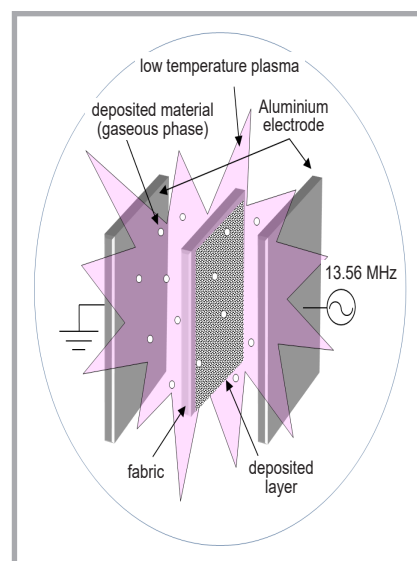- three variants of vapours flow rate: 0.016, 0.032 and 0.064 Pa m³ s⁻¹,

Figure 1. *Idea of the surface modification of ballistic textiles using PACVD [13].*

Table 3. *List of conditions of the synthesis and deposition of organosilane coatings on p-aramid substrates as well as on fibrous sheets made of UHMWPE fibres.*

Type of monomer	Monomer flow rate, Pa·m³·s⁻¹ (in sccm)	Carrier gas flow rate, Pa·m³·s⁻¹ (in sccm)	Power, W	Time period of deposition, min	Sample
HMDSO	0.008 (5)	-	50	3	HMDSO/5sccm/50W/3min
	0.016 (10)	-	50	1	HMDSO/10sccm/50W/1min
				3	HMDSO/10sccm/50W/3min
			100	1	HMDSO/10sccm/100W/1min
				3	HMDSO/10sccm/100W/3min
	0.032 (20)	-	50	1	HMDSO/20sccm/50W/1min
				3	HMDSO/20sccm/50W/3min
			100	1	HMDSO/20sccm/100W/1min
				3	HMDSO/20sccm/100W/3min
	0.016 (10)	O₂; 0.08 (50)	100	1	O2/50sccm/ HMDSO/10sccm/100W/1min
				3	O2/50sccm/ HMDSO/10sccm/100W/3min
				5	O2/50sccm/ HMDSO/10sccm/100W/5min
			200	3	O2/50sccm/ HMDSO/10sccm/200W/3min
	0.032 (20)	O₂; 0.16 (100)	100	3	O2/100sccm/ HMDSO/20sccm/100W/3min
			200	3	O2/100sccm/ HMDSO/20sccm/200W/3min
	0.032 (20)	O₂; 0.32 (200)	100	3	O2/200sccm/ HMDSO/20sccm/100W/3min
			200	3	O2/200sccm/ HMDSO/20sccm/200W/3min
	0.032 (20)	O₂; 0.48 (300)	100	3	O2/300sccm/ HMDSO/20sccm/100W/3min
			200	3	O2/300sccm/ HMDSO/20sccm/200W/3min
	0.016 (10)	Ar; 0.12 (75)	50	1	Ar/75sccm/ HMDSO/10sccm/50W/1min
				3	Ar/75sccm/ HMDSO/10sccm/50W/3min
			100	3	Ar/75sccm/ HMDSO/10sccm/100W/3min
	0.032 (20)	Ar; 0.24 (150)	100	3	Ar/150sccm/ HMDSO/20sccm/100W/3min
			200	3	Ar/150sccm/ HMDSO/20sccm/200W/3min
	0.032 (20)	Ar; 0.48 (300)	100	3	Ar/300sccm/ HMDSO/20sccm/100W/3min
			200	3	Ar/300sccm/ HMDSO/20sccm/200W/3min
	0.032 (20)	Ar; 0.64 (400)	100	3	Ar/400sccm/ HMDSO/20sccm/100W/3min
			200	3	Ar/400sccm/ HMDSO/20sccm/200W/3min

■ time period of plasma operation on the substrates: from 1 and 3 min.

The programme of deposition conditions is listed in **Table 2**.

The organosilane coatings were made in the plasma of the following monomer vapours: Hexamethyldisiloxane (HMDSO) $C_6H_{18}OSi_2$.

A 4-stage procedure of the process was established:
■ 30 min. deaeration of the sample,
■ activation in the process gas,
■ deposition of polymer coating,
■ 30 min. sample conditioning under a vacuum after the process.

The plasma was excited in monomer vapours with the following technical conditions:
■ with and without a carrier gas. Two kinds of gas were applied: argon and oxygen,
■ two variants of power applied to the reactor: 100 and 200 W,
■ several variants of the flow rate of the monomer and carrier gases,

■ time period of the plasma operation on the substrates: from 1 to 3 min.

Deposition conditions are listed in *Table 3*.

Analytical methods

ATR-FTIR
Tests were performed with a single beam spectrophotometer FTIR–Nicolet 6700 (THERMO Scientific, USA) by the single-reflection method at the following settings of the device work parameters:
■ DTGS KBr detector,
■ measuring range: 4000 - 600 cm⁻¹,
■ accuracy of measurement recording: 2 cm⁻¹,
■ mirror speed: 0.31 mm/s,
■ aperture: 50,
■ minimum number of scans recorded: 32 for each measurement.

Auxiliary devices:
■ reflective snap of ITR type (Thermo Scientific) with diamond crystal of a reflection angle of 45°,
■ PC computer with OMNIC 8.0.380 software, equipped with libraries of spectra for processing and analysing the spectroscopic spectra.

The starting point for research with the ATR technique was cutting out a strip of textile material with dimensions of 20×20 mm and applying it onto the Dia crystal with an appropriate force. For complete measurement, two are to be performed: the spectrum of the background (the crystal) and that of the crystal with a sample. Measurement of the background, which is recorded in the internal memory of the spectrophotometer, is automatically subtracted during sample measurement, in this way eliminating the impact of external conditions on the results of the research. In addition, atmospheric correction was performed and ATR correction of spectra at a wavelength of 1000 cm⁻¹.

The resulting spectra were analysed using a PC equipped with the program OMNIC 8.0.380 for analysing the spectroscopic spectra. The chemical structure of the sample material was determined based on an analysis of absorption bands. The rate of HMDSO deposition, differentiated by using carrier gas oxygen and argon, was determined based on the changes of intensity of the absorption bands correlated with the chemical groups at wave numbers of 822 cm⁻¹

(–Si–0–Si), 1050 cm^{-1} (1016 cm^{-1}) (Si–CH$_2$–Si), 1252 cm^{-1} (Si–CH$_3$) and 2957 cm^{-1} (Si–CH$_3$). Absorbance quotients K_1 and K_2 were calculated for selected bands in order to determine the chemical composition of the layers applied according to the formulas:

$$K_1 = A_{1016}/A_{1252} \text{ and}$$
$$K_2 = A_{1252} / A_{2957}$$

Then optimum variants were selected on the basis of maximum values of absorbance quotients of the bands mentioned as a deposition indicators of the silicon compounds. At a later stage, the effects of the HMDSO deposition were compared on the basis of changes in absorbance of the above-mentioned absorption bands using carrier gases of oxygen and argon to esablish the effects of HMDSO deposition without the use of these gases. Moreover besides the absorption bands mentioned, for the samples of sheets of fibrous material Dyneema® exposed to the HMDSO processing with the presence of oxygen as the carrier gas, the formation of a new absorption band was observed at wavenumber λ = 3450 cm^{-1} correlated with the –OH group.

Morphological studies with elemental microanalysis of the chemical composition using the SEM/EDS technique

Chemical and morphological analysis of the surface modified woven fabrics were carried out by means of a scanning electron microscope (SEM) - Nova NanoSEM 230 from FEI company (SE Detector, High Voltage: 10 kV, Low Vacuum) with X-ray microanalyser EDS (Energy-dispersive X-ray Spectroscopy) from EDAX (Detector SDD, energy resolution: Mn 132 eV). A quantitative chemical analysis of the studied fibrous materials studied was carried out by the use of ViP Quant software with ZAF and low vacuum correction procedures. The samples were prepared by fixing the fibrous materials to a holder with a conductive carbon adhesive tape.

■ Results and discussion

The synthesis and deposition of polymeric layers were performed with the PACVD method on fibrous substrates of p-aramid (woven fabrics of Kevlar fibres) and polyethylene (fibrous sheets of UHMWPE). According to the assumptions, the selection of the type of polymer for deposition on substrates was made in terms of giving the substrates the following specific surface properties: barrier, hydrophobic and tribological. The synthesis was performed for two types of plasma polymers: based on vapours of organofluorine and organosilane monomers. Furthermore at the initial stage of works, activation of the substrate surfaces was assumed in an environment of low temperature plasma with various process gases, ensuring proper adhesion of the coatings created.

ATR-FTIR analysis

In the ATR-FTIR research it was found that the degree of deposition of the fluorine compound is greatest for processing variants in the following order from the largest:
- F/40sccm/100W/3min,
- F/40sccm/200W/1min,
  F/40sccm/250W/3min,
  F/20sccm/200W/3min,
- F/40sccm /200W/3min,
  F/10sccm/200W/3min.

In other variants, ATR-FTIR spectra analysis did not show any presence of fluorine compounds deposited onto the sample of fabric Style 363/120.

The cumulative ATR-FTIR spectra of modified fabrics Style 363/120 are presented on *Figure 2* (see page 106).

The largest degree of fluorine compound deposition on the sample of Dyneema® SB51 was found for the variant of processing in the order:
- F/40sccm/250W/3min,
- F/40sccm/200W/1min and
  F/40sccm/100W/3min.

In other variants, the ATR-FTIR spectra analysis did not show any presence of fluorine compounds deposited onto the samples of Dyneema® SB51.

The cumulative ATR-FTIR spectra of modified fibrous sheets of Dyneema® SB51 are presented in the *Figure 3* (see page 106).

The cumulative ATR-FTIR spectra of Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO are presented in *Figure 4* (see page 107).

The absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for Style 363/120 woven fabrics are presented in *Table 4* (see page 107).

Cumulative ATR-FTIR bands of the Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO with the use of O$_2$ as a carrier gas are presented in *Figure 5* (see page 108).

Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO and with the use of oxygen as a carrier gas are presented in *Table 5* (see page 108).

Cumulative ATR-FTIR spectra of Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO and with the use of Ar as the carrier gas are presented in *Figure 6* (see page 109). Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) for Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO and with the use of Ar as the carrier gas are listed in *Table 6* (see page 109).

Cumulative ATR-FTIR spectra of fibrous sheets of Dyneema® SB51 material of UHMWPE fibres modified with low-temperature plasma in the presence of HMDSO are presented on *Figure 7* (see page 110).

Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for the modified fibrous sheets of Dyneema® SB51 material of UHMWPE fibres are presented in *Table 7* (see page 110).

Cumulative ATR-FTIR spectra of fibrous sheets of Dyneema® SB51 material of UHMWPE fibres, modified with low-temperature plasma in the presence of HMDSO and with the use of O$_2$ as a carrier gas are presented on *Figure 8* (see page 111).

Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for the fibrous sheets of Dyneema® SB51 material of UHMWPE fibres
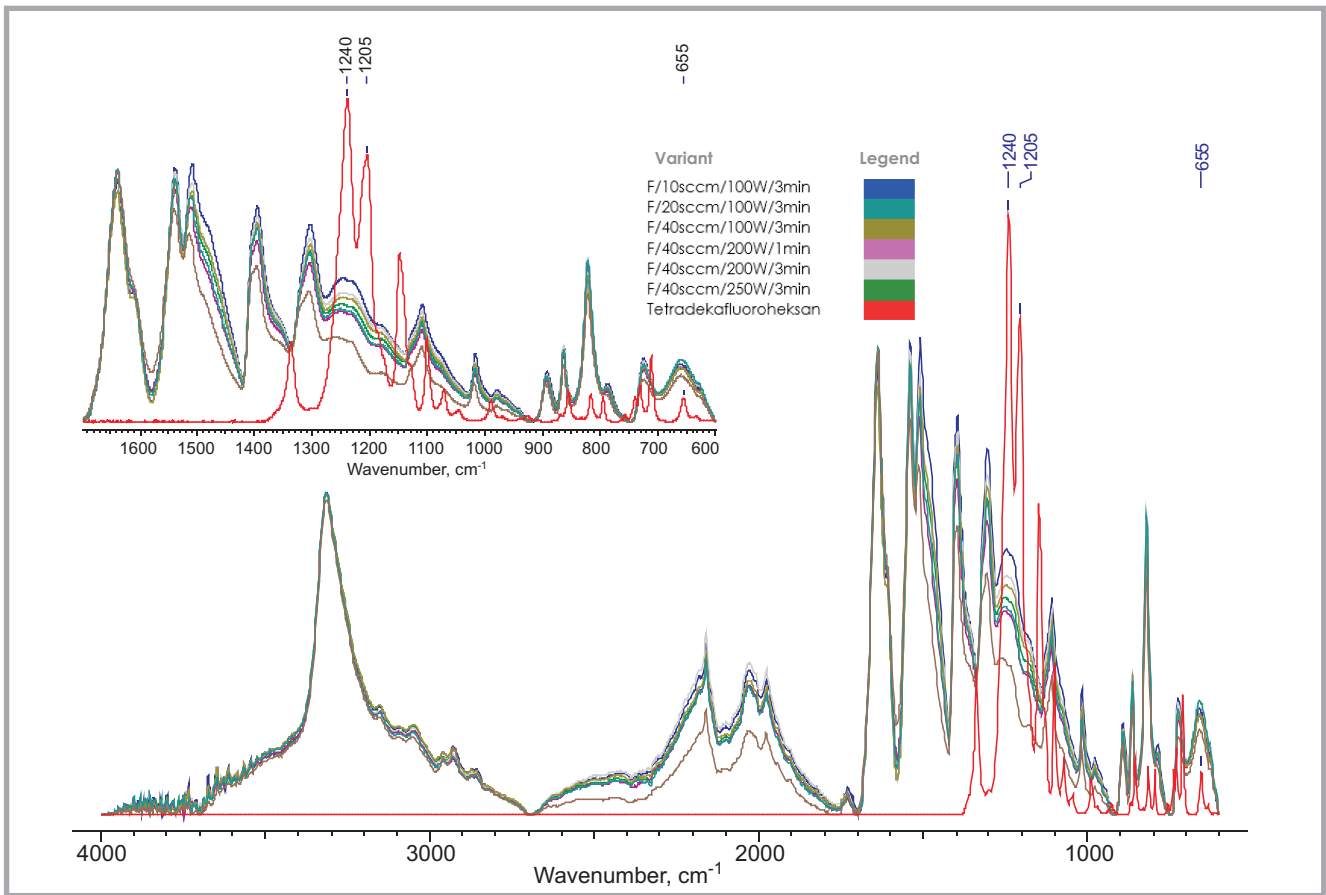
Figure 2. *ATR-FTIR spectra of Style 363/120 fabrics modified with low-temperature plasma in the presence of TDFH under various processing conditions in relation to the TDFH spectrum.*
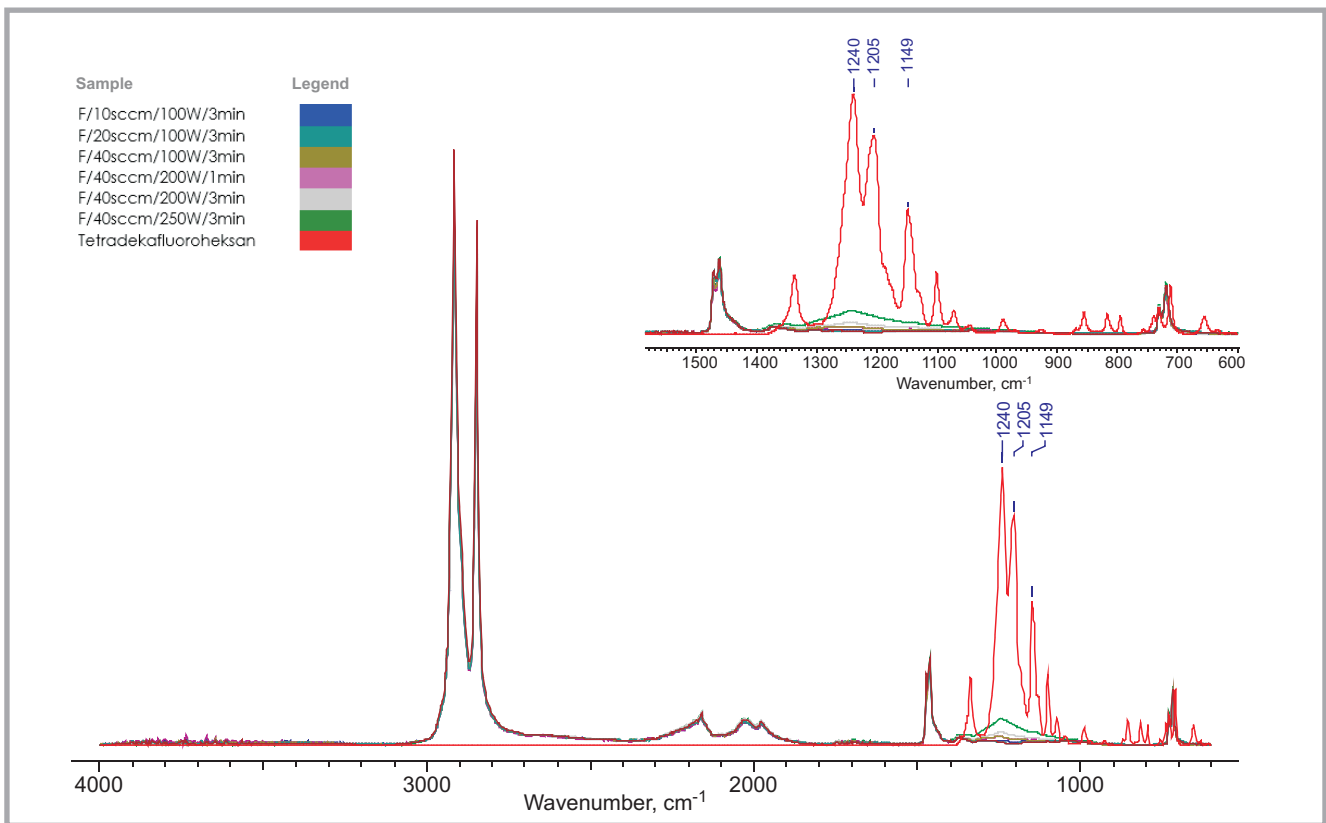

Figure 3. *ATR-FTIR spectra of fibrous sheets of Dyneema® SB51 modified with low-temperature plasma in the presence of TDFH under various processing conditions in relation to the TDFH spectrum.*
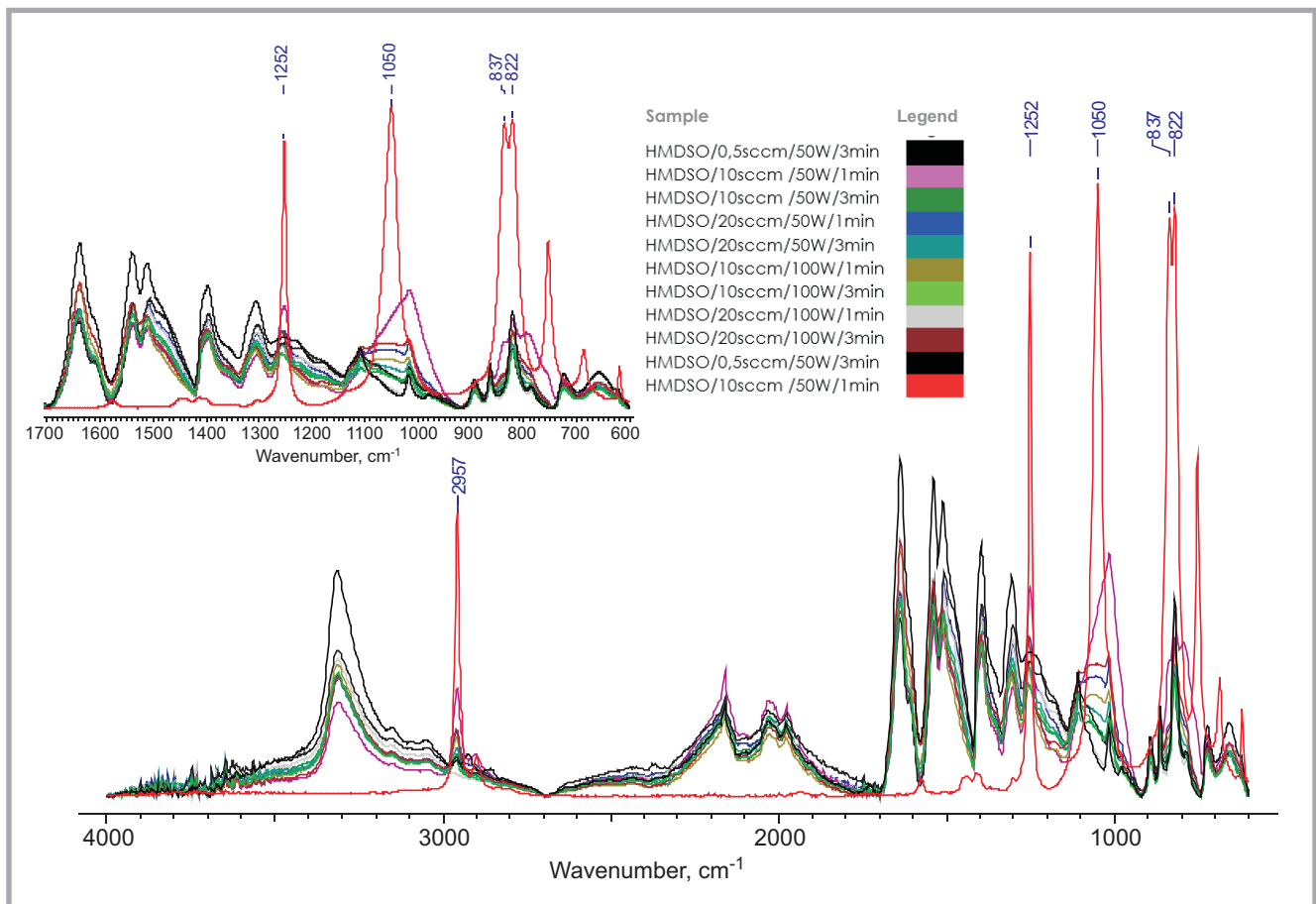
Figure 4. *ATR-FTIR spectra of Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO in relation to the HMDSO spectrum.*

Table 4. *Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for Style 363/120 woven fabrics.*

Variant of processing	Position of the absorption band, cm⁻¹ Absorbance				Quotients of absorbance of characteristic bands	
	822	1050 (1016)	1252	2957	$K_1 = A_{1016}/A_{1252}$	$K_2 = A_{1252}/A_{2957}$
HMDSO/0,5sccm/50W/3min	0.144	0.125	0.149	0.062	0.839	2.403
HMDSO/10sccm /50W/1min	0.118	0.055	0.101	0.017	0.545	5.941
HMDSO/10sccm /50W/3min	0.110	0.068	0.103	0.039	0.660	2.641
HMDSO/20sccm/50W/1min	0.111	0.072	0.106	0.034	0.679	3.118
HMDSO/20sccm/50W/3min	0.148	0.131	0.145	0.062	0.903	2.339
HMDSO/10sccm/100W/1min	0.112	0.078	0.125	0.036	0.624	3.472
HMDSO/10sccm/100W/3min	0.123	0.087	0.121	0.045	0.719	2.689
HMDSO/20sccm/100W/1min	0.145	0.098	0.121	0.055	0.810	2.200
HMDSO/20sccm/100W/3min	0.172	0.226	0.195	0.100	1.159	1.950
HMDSO	0.550	0.573	0.508	0.267	1.128	1.903

modified with low-temperature plasma in the presence of HMDSO and with the use of O₂ as a carrier gas are presented in ***Table 8*** (see page 111).

Cumulative ATR-FTIR spectra of fibrous sheets of Dyneema® SB51 material of UHMWPE fibres modified with low-temperature plasma in the presence of HMDSO and with the use of Ar, as the carrier gas are presented on ***Figure 9*** (see page 112).

Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for fibrous sheets of Dyneema® SB51 material of UHMWPE fibres modified with low-temperature plasma in the presence of HMDSO and with the use of Argon as the carrier gas are presented in ***Table 9*** (see page 112).

The plasma polymer p-(HMDSO) is used for reducing the surface free energy, water vapour and oxygen permeability through the polymeric substrates onto which it was deposited. Our aim was to obtain durable p-(HMDSO) coatings of silicon oxide free from defects, with a small number of granules, hydrophobic for various types of textile materials, and differing in structure and chemical composition. From the papers published on the plasma polymerisation of this polymer it is known that the glow discharge parameters decide what layers are created: soft (with a high content of methyl and methylene groups), hard and brittle,
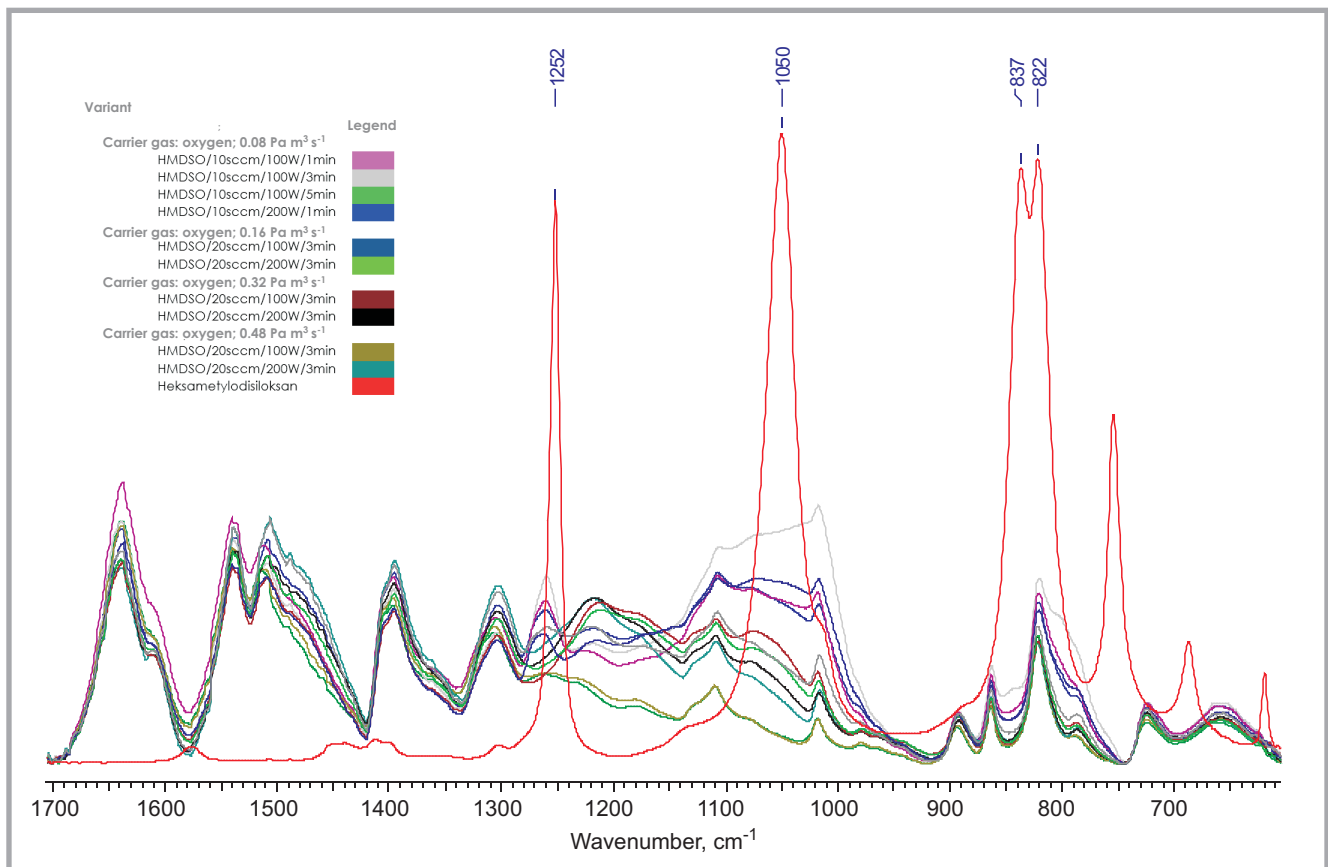
Figure 5. *ATR-FTIR spectra (within the wave-number range from 1700 cm^{-1} to 600 cm^{-1}) of Style 802/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO and with the use of O$_2$ as a carrier gas in relation to the HMDSO spectrum.*

Table 5. *Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO and with the use of oxygen as a carrier gas.*

Variant of processing		Position of the absorption band, cm^{-1} Absorbance				Quotients of absorbance of characteristic bands	
Carrier gas: Oxygen, Pa·m^3·s^{-1}	Sample	822	1050 (1016)	1252	2957	$K_1 = A_{1016}/A_{1252}$	$K_2 = A_{1252}/A_{2957}$
0.08	HMDSO/10sccm/100W/1min	0.016	0.125	0.040	0.111	3.125	0.360
	HMDSO/10sccm/100W/3min	0.054	0.148	0.155	0.155	0.955	1.000
	HMDSO/10sccm/100W/5min	0.068	0.170	0.234	0.168	0.726	1.393
	HMDSO/10sccm/200W/1min	0.023	0.081	0.041	0.109	1.976	0.376
	HMDSO/10sccm/200W/3min	0.047	0.140	0.145	0.147	0.966	0.986
0.16	HMDSO/20sccm/100W/3min	0.033	0.124	0.099	0.124	1.253	0.798
	HMDSO/20sccm/200W/3min	0.041	0.118	0.168	0.139	0.702	1.209
0.32	HMDSO/20sccm/100W/3min	0.031	0.140	0.076	0.116	1.842	0.655
	HMDSO/20sccm/200W/3min	0.027	0.147	0.083	0.111	1.771	0.748
0.48	HMDSO/20sccm/100W/3min	0.029	0.151	0.065	0.115	2.323	0.565
	HMDSO/20sccm/200W/3min	0.024	0.150	0.067	0.112	2.239	0.598
-	HMDSO	0.550	0.573	0.508	0.267	1.128	1.903

with the participation of granules, or homogeneous of repetitive composition.

For this reason, various approaches were used - A glow discharge was excited in vapours of monomer HMDSO (100%) in a mixture of inert carrier gas (Ar) with the monomer as well as in a carrier gas mixture rich in oxygen (O$_2$) with a monomer in order to reduce the content of carbon atoms.

In this case, the results of studies assessed by the ATR-FTIR technique

are a very important tool for assessing the layers. *Table 10* (see page 112) lists the main absorption bands which identify the polymer.

A stronger absorption within the band range of 1000 cm^{-1} - 1150 cm^{-1} may indicate an increase in the Si-O-Si group number, while for absorption in the 1260 cm^{-1} band, there is occurrence of Si-CH$_3$ groups, and the absorption in 1260 cm^{-1} band - the presence of CH$_x$ groups [2 - 5].

Two numerical indicators: K$_1$ & K$_2$ were adopted as a tool to deduce the chemical structure of p (HMDSO).

$K_1 = A_{\text{Si-O-Si } (\lambda = 1016 \text{ cm}^{-1})}/A_{\text{Si-CH}_3 (\lambda = 1252 \text{ cm}^{-1})}$;

An increase in the K$_1$ index is related to that in the Si-O-Si group number in relation to Si-CH$_3$. On this basis this supposition, it seems reasonable that the content of carbon atoms is linked to the decrease in silicon atoms - hence a coating similar in structure to SiO$_2$ is formed.
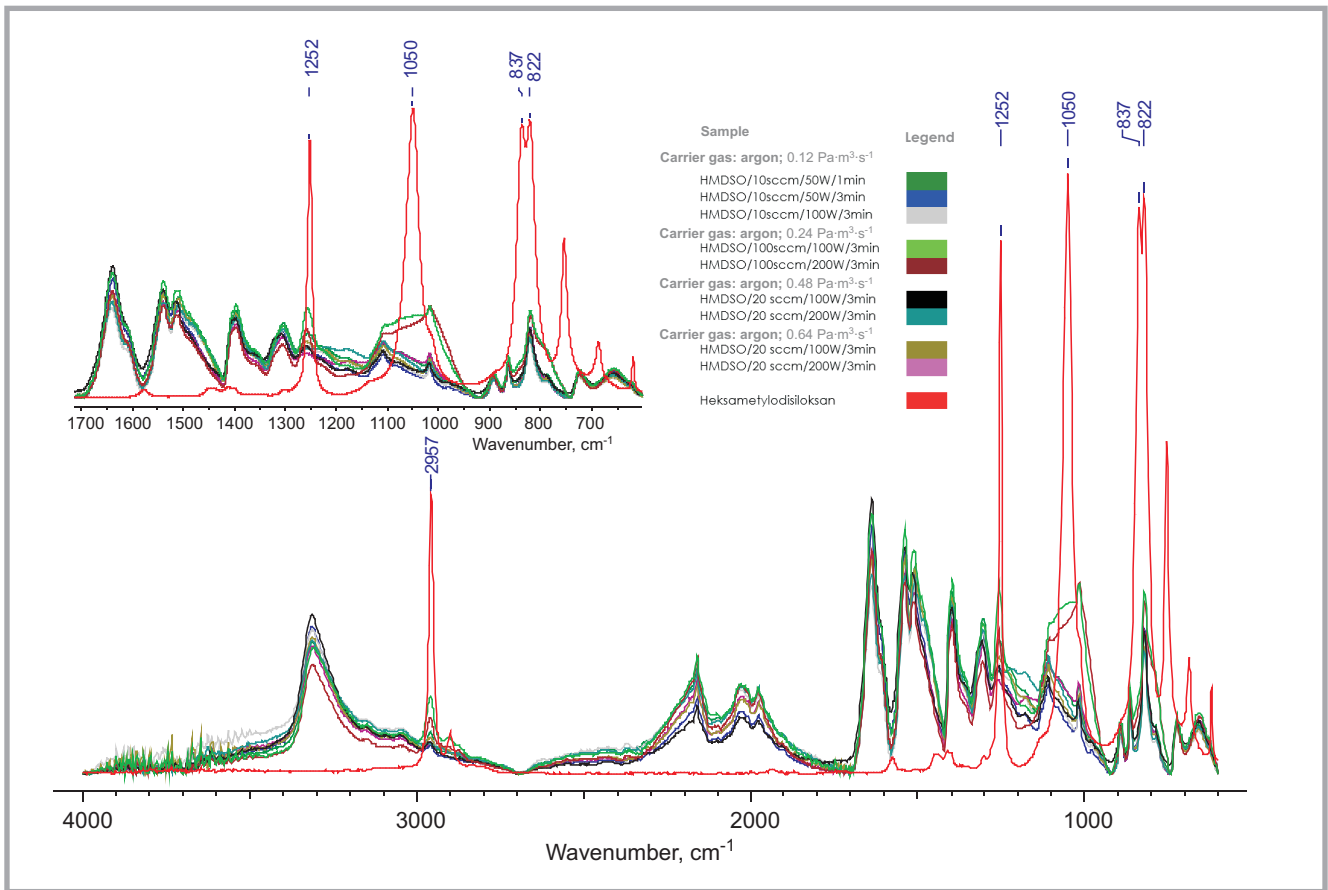
Figure 6. *ATR-FTIR spectra of Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO and with the use of Ar as the carrier gas in relation to the HMDSO spectrum*

Table 6. *Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for Style 363/120 woven fabrics modified with low-temperature plasma in the presence of HMDSO and with the use of Ar as the carrier gas.*

Variant of processing		Position of the absorption band, cm⁻¹ Absorbance				Quotients of absorbance of the characteristic bands	
Carrier gas: Argon; Pa m³ s⁻¹	Sample	822	1050 (1016)	1252	2957	$K_1 = A_{1016}/A_{1252}$	$K_2 = A_{1252}/A_{2957}$
0.12	HMDSO/10sccm/50W/1min	0.133	0.084	0.127	0.039	0.661	3.256
	HMDSO/10sccm/50W/3min	0.139	0.063	0.103	0.027	0.612	3.815
	HMDSO/10sccm/100W/3min	0.112	0.061	0.104	0.034	0.587	3.059
0.24	HMDSO/100sccm/100W/3min	0.164	0.182	0.137	0.053	1.328	2.585
	HMDSO/100sccm/200W/3min	0.174	0.181	0.178	0.073	1.017	2.438
0.48	HMDSO/20 sccm/100W/3min	0.135	0.068	0.102	0.030	0.667	3.400
	HMDSO/20 sccm/200W/3min	0.118	0.071	0.098	0.126	0.724	0.778
0.64	HMDSO/20 sccm/100W/3min	0.120	0.076	0.111	0.034	0.685	3.265
	HMDSO/20 sccm/200W/3min	0.136	0.087	0.090	0.030	0.967	3.000
-	HMDSO	0.550	0.573	0.508	0.267	1.128	1.903

$$K_2 = \frac{A_{Si\text{-}CH_3(\lambda = 1252 \text{ cm}^{-1})}}{A_{CH_x (\lambda = 2900\text{-}2960 \text{ cm}^{-1})}}$$

A decrease in the K_2 index may mean a decrease in the number of Si-CH₃ groups with the time of PACVD processing in relation to the total number of bonds (λ = 2900 cm⁻¹), which indicates a strong fragmentation of the monomer (breaking of SiCH₃ bonds, recombination and creation of C-C bonds).

Analysis of indices K_1 and K_2 compiled leads to interesting conclusions:

A. for p(HMDSO) polymeric coatings created without carrier gases the following is observed:
- with an increase in the time period of deposition from 1 to 3 min. the value of K_1 increases (the number of carbon atoms linked to the silicon atoms decreases – a coating similar in structure to SiO_2 is formed). At the same time, a decrease in the K_2 index is observed - which indicates strong fragmentation of the monomer (breaking SiCH₃ bonds and recombination as well as forming C-C bonds).

- with an increase in the power applied K_2 decreases – which indicates progressive fragmentation of the monomer. This behaviour is confirmed by the results of SEM-EDS research.

B. for the p(HMDSO) polymeric coatings created with Ar as a carrier gas the following is observed:
- with an increase in the power applied the K_2 index decreases – which indicates progressive fragmentation of the monomer. This behaviour is confirmed by the results of SEM-EDS re-
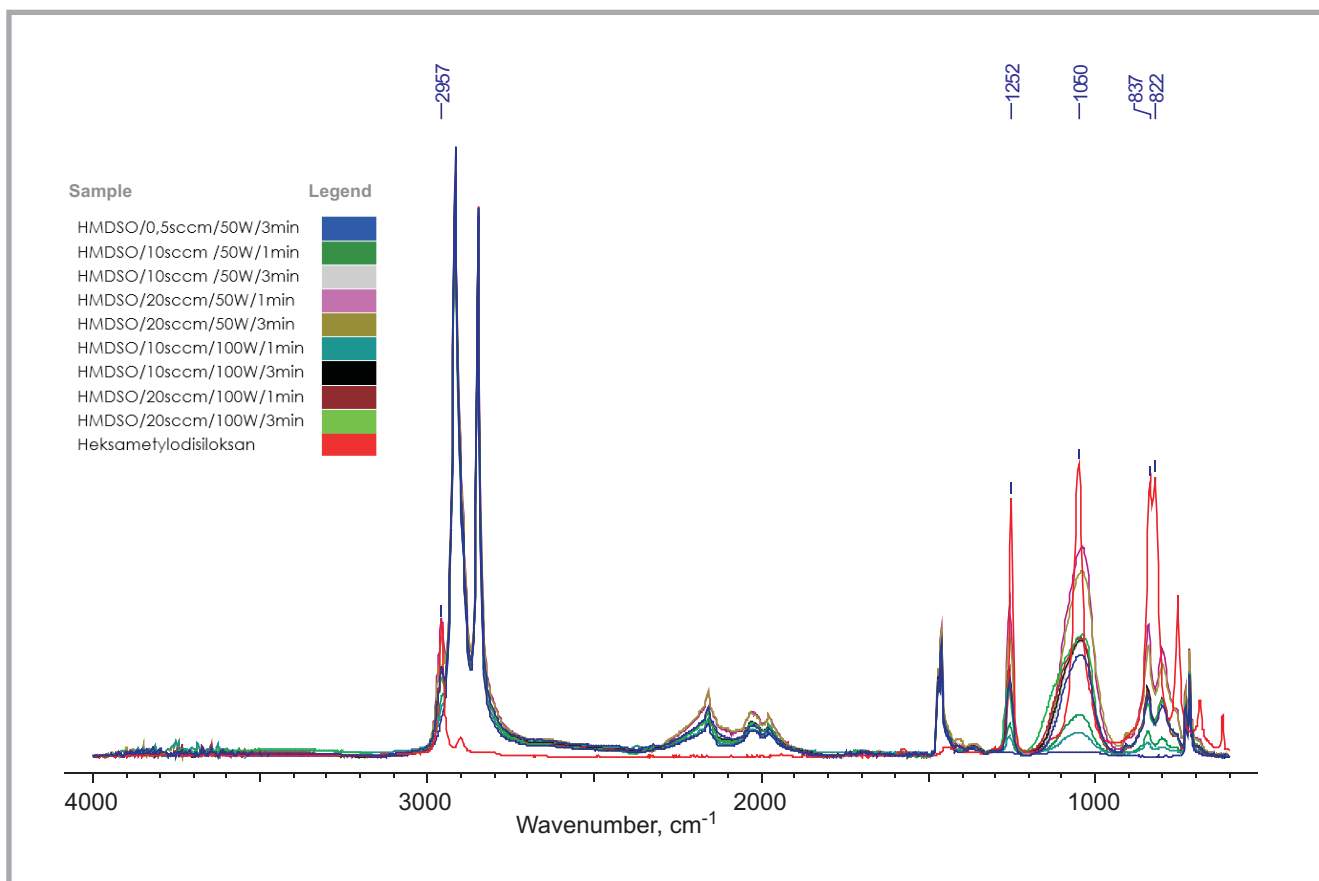
Figure 7. *ATR-FTIR spectra of fibrous sheets of Dyneema® SB51 material of UHMWPE fibres modified with low-temperature plasma in the presence of HMDSO, related to the HMDSO spectrum.*

Table 7. *Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for the modified fibrous sheets of Dyneema® SB51 material of UHMWPE fibres.*

Variant of processing	Position of absorption band, cm⁻¹ Absorbance				Quotients of absorbance of characteristic bands	
	822	1050 (1016)	1252	2957	$K_1 = A_{1016}/A_{1252}$	$K_2 = A_{1252}/A_{2957}$
HMDSO/0,5sccm/50W/3min	0.099	0.200	0.145	0.172	1.379	0.843
HMDSO/10sccm /50W/1min	0.036	0.082	0.063	0.122	1.302	0.516
HMDSO/10sccm /50W/3min	0.111	0.240	0.170	0.154	1.412	1.104
HMDSO/20sccm/50W/1min	0.112	0.233	0.167	0.169	1.395	0.988
HMDSO/20sccm/50W/3min	0.114	0.228	0.169	0.177	1.349	0.955
HMDSO/10sccm/100W/1min	0.019	0.047	0.040	0.096	1.175	0.417
HMDSO/10sccm/100W/3min	0.182	0.365	0.246	0.235	1.484	1.047
HMDSO/20sccm/100W/1min	0.210	0.411	0.294	0.271	1.398	1.085
HMDSO/20sccm/100W/3min	0.115	0.225	0.147	0.182	1.531	0.808
HMDSO	0.550	0.573	0.508	0.267	1.128	1.903

search. The K_1 index increases, hence a coating with a structure similar to SiO_2 is created.

■ with a decrease in Ar flow, the K_1 index increases – a coating with a structure similar to SiO_2 is created, the behaviour of which is confirmed by the results of SEM-EDS research on the chemical composition of the coating.

C. for p(HMDSO) polymeric coatings created with O_2 as a carrier gas, no logical change in the K_1 and K_2. indices was observed.

SEM-EDS analysis

Figures 10 - 11 (see page 113) present, respectively, the dependences of the surface composition in % content of p-aramid Style 363/120 woven fabric as well as fibrous sheets of Dyneema SB51 material on the parameters of the modification process with low-temperature plasma in the presence of TDFH vapours.

The fabrics examined were uniformly coated with fluorine in the range of 0.8% - 5.9% depending on the process parameters. The microscopic evaluation did

not show any significant morphological changes in the structure of the fibres. An increase in the flow of the monomer under low-temperature plasma induced an increase in fluorine, determined with the EDS method on the surface of samples of p-aramid fabrics. A similar effect was observed with an increase in power and prolonged processing with plasma. The samples were also assessed for the presence of Sodium and Sulphur originating probably from the auxiliary compounds co-existing on the fabric surfaces and introduced as agents for fa-
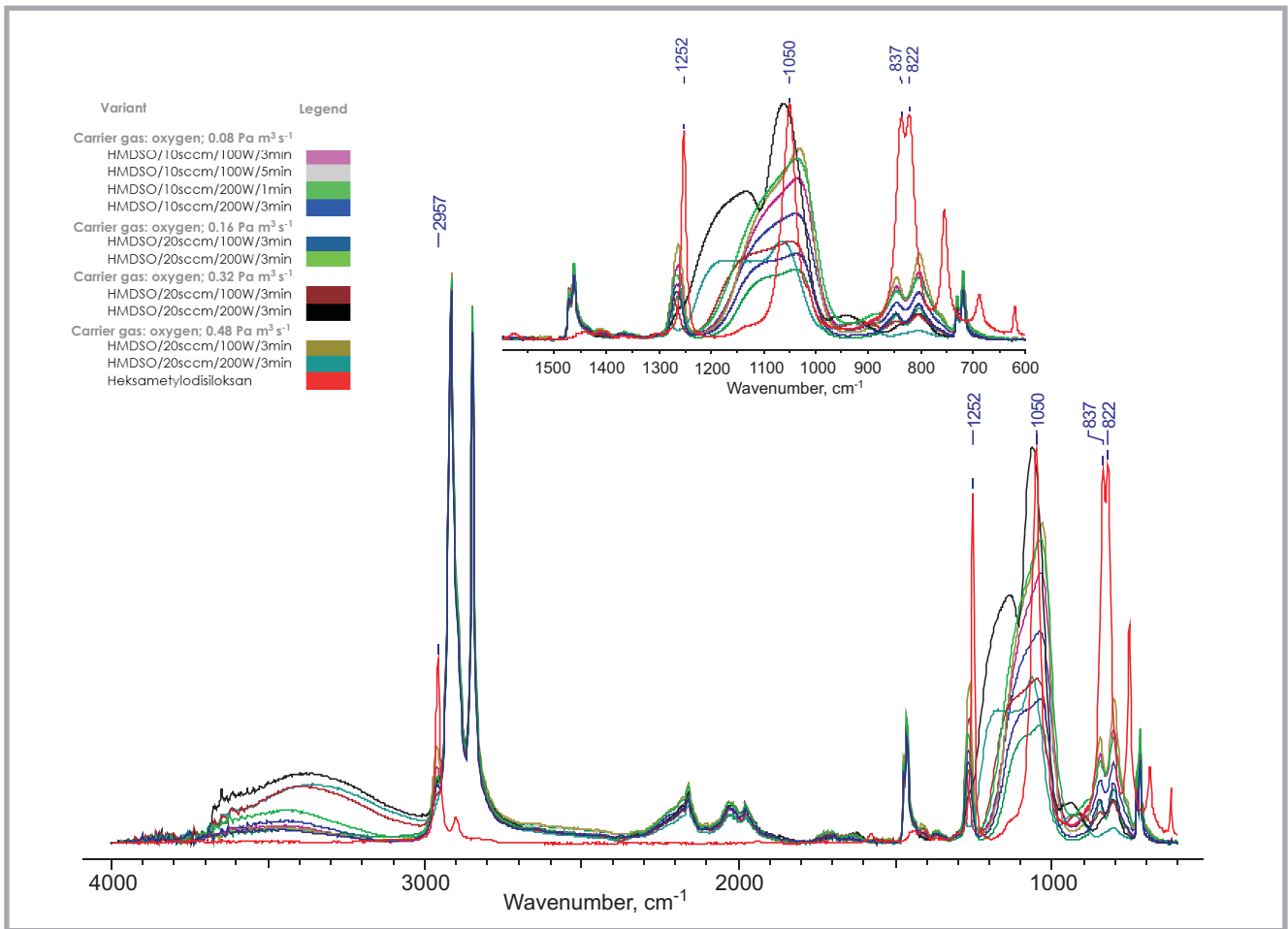
Figure 8. *ATR-FTIR spectra of fibrous sheets of Dyneema® SB51 material of UHMWPE fibres, modified with low-temperature plasma in the presence of HMDSO and with the use of Oxygen as a carrier gas, related to HMDSO spectrum.*

Table 8. *Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for fibrous sheets of Dyneema® SB51 material of UHMWPE fibres modified with low-temperature plasma in the presence of HMDSO and with the use of Oxygen as a carrier gas.*

Variant of processing		Position of the absorption band, cm⁻¹ Absorbance				Quotients of absorbance of characteristic bands	
Carrier gas: Oxygen, Pa m³ s⁻¹ (in sccm)	Sample	822	1050 (1016)	1252	2957	$K_1 = A_{1016}/A_{1252}$	$K_2 = A_{1252}/A_{2957}$
0.08 (10)	HMDSO/10sccm/100W/1min	0.061	0.133	0.098	0.064	0.015	1.357
	HMDSO/10sccm/100W/3min	0.165	0.393	0.181	0.111	0.026	2.171
	HMDSO/10sccm/100W/5min	0.209	0.462	0.229	0.139	0.022	2.017
	HMDSO/10sccm/200W/1min	0.079	0.172	0.107	0.096	0.021	1.607
	HMDSO/10sccm/200W/3min	0.116	0.307	0.135	0.094	0.033	2.274
0.16 (20)	HMDSO/20sccm/100W/3min	0.088	0.210	0.118	0.085	0.019	1.780
	HMDSO/20sccm/200W/3min	0.153	0.441	0.158	0.097	0.048	2.791
0.32 (	HMDSO/20sccm/100W/3min	0.061	0.240	0.103	0.074	0.083	2.330
	HMDSO/20sccm/200W/3min	0.064	0.576	0.075	0.091	0.102	7.680
0.48	HMDSO/20sccm/100W/3min	0.057	0.218	0.041	0.020	0.029	5.317
	HMDSO/20sccm/200W/3min	0.023	0.241	0.040	0.063	0.085	6.025
-	HMDSO	0.550	0.573	0.508	0.267	1.128	1.903

cilitating yarn treatment during weaving processes.

A similar phenomenon was observed on samples of fibrous sheets of Dyneema® SB51 material, where with an increase in the power applied and prolonged processing the amount of fluorine assessed with the EDS technique increased. It covered homogenously all the surface of the material examined.

As a result of the surface processing, a relatively high content of Oxygen was also observed, which may originate from post-processing oxidation of the low- molecular binder of the Dyneema® SB51 composite.

Figures 12 & ***13*** (see page 113 &114) present, respectively, the dependencies in % content of the composition of the surface of p-aramid Style 363/120 woven fabric and fibrous sheets of
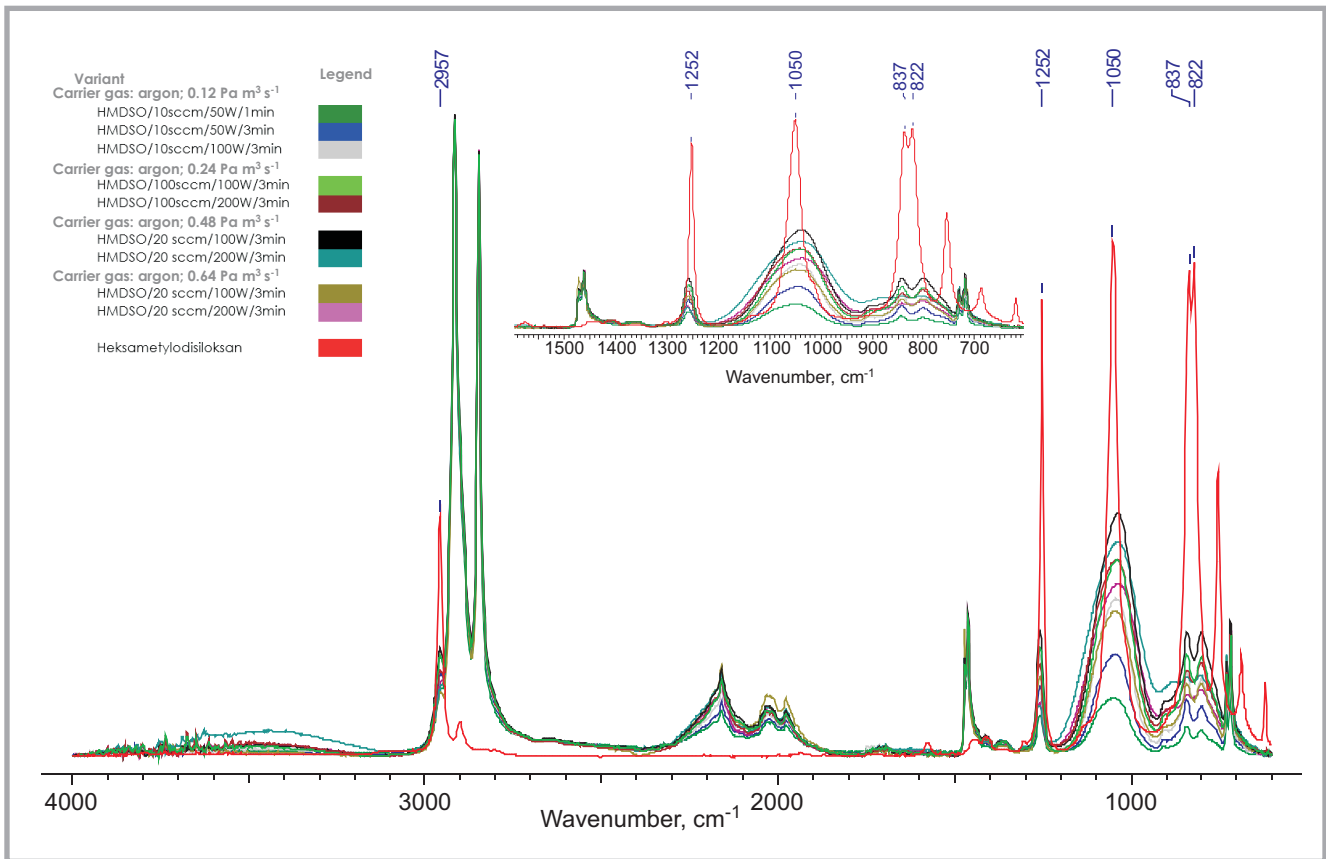
Figure 9. ATR-FTIR spectra of fibrous sheets of Dyneema® SB51 material of UHMWPE fibres modified with low-temperature plasma in the presence of HMDSO and with the use of Ar as the carrier gas in relation to the HMDSO spectrum

Table 9. Absorbance values of characteristic absorption bands originating from hexamethyldisiloxane (HMDSO) and their quotients for fibrous sheets of Dyneema® SB51 material of UHMWPE fibres modified with the low-temperature plasma in the presence of HMDSO, and with the use of Argon as the carrier gas

Variant of processing		Position of the absorption band, cm⁻¹ Absorbance				Quotients of absorbance of characteristic bands	
Carrier gas: Argon, Pa m³ s⁻¹	Sample	822	1050 (1016)	1252	2957	$K_1 = A_{1016}/A_{1252}$	$K_2 = A_{1252}/A_{2957}$
0.12	HMDSO/10sccm/50W/1min	0.028	0.065	0.045	0.076	1.444	0.592
	HMDSO/10sccm/50W/3min	0.055	0.113	0.077	0.093	1.468	0.828
	HMDSO/10sccm/100W/3min	0.087	0.175	0.110	0.114	1.591	0.965
0.24	HMDSO/100sccm/100W/3min	0.110	0.218	0.121	0.111	1.802	1.090
	HMDSO/100sccm/200W/3min	0.104	0.218	0.103	0.095	2.117	1.084
0.48	HMDSO/20 sccm/100W/3min	0.139	0.270	0.137	0.118	1.971	1.161
	HMDSO/20 sccm/200W/3min	0.090	0.239	0.057	0.081	4.193	0.704
0.06	HMDSO/20 sccm/100W/3min	0.081	0.161	0.088	0.072	1.830	1.222
	HMDSO/20 sccm/200W/3min	0.075	0.192	0.060	0.084	3.200	0.714
-	HMDSO	0.550	0.573	0.508	0.267	1.128	1.903

Dyneema® SB51 material on the parameters of the modification process with low-temperature plasma in the presence of HMDSO vapours.

It is remarkable that in the case of the modification of p-aramid Style 363/120 woven fabrics, the highest content of silicon on the surface of the said textile materials was found when low flows of carrier gas were applied. The introduction of argon as the carrier gas caused an increase in EDS-detectable quantities of silicon, the density of which decreased with an increase in the flow of the carrier gas - argon. In the case of using oxygen as the carrier gas - the silicon content increased with an increase in the applied power and with a reduction in the flow of the carrier gas. In the presence of only the substrate's vapours during low-temperature plasma treatment - the highest values of silicon deposited

Table 10. Absorption bands in the ATR-FTIR spectrum characteristic for HMDSO [14 - 17].

Absorption band, cm⁻¹	Bond	Nature of band
1000-1150	Si-O-Si	asymmetric stretching
800	Si-O-Si Si-C CH3	deformative stretching CH₃ deformative in Si-(CH₃)₂
840	Si- CH3	deformative
1260	CH3	symmetric bending in Si-CH3
2900-2960	CH_x	symmetric and asymmetric, stretching

on the surface of the material samples were determined after a longer process of modification. Similar to the fluoropolymer depositions, the presence of Al, S and Na originating from the auxiliary agents wasdetected.

The highest contents of silicon on the surface of the modified sheets of Dyneema® SB51 fibrous material were determined for the samples processed in a 3 min time period. The introduction of oxygen as the carrier gas resulted in a reduction in the Si content on the surface of a sheet with an increasing gas flow rate. In the case of using argon as the carrier gas, decreasing its flow rate and increasing the power applied caused a reduction in the content of silicon on the sample surface. That phenomenon was significantly different than those observed with p-aramid fabrics, which may indicate a dependence of the result of the deposition on the chemical composition and topography of the textile medium.

The structures obtained observed on the surface of the modified fibrous sheets are the closest to the ratio of SiO_2, of the samples modified in the presence of oxygen (Dyneema® SB51 $O_2/0.16 Pam^3 s^{-1}/HMDSO/0.032 Pam^3 s^{-1}/200W/3min$) or argon (samples modified at high flows of carrier gas 0.48 – 0.64 Pa m^3 s^{-1}) used as the carrier gases.

The topography of the fibrous materials modified is shown in ***Figure 14*** (see page 114).

The surface topography of the PACVD modified textiles has not changed during the process of polymer deposition. The PACVD process with TDFH has not introduced any deformations and destructions of single fibres. Moreover, the PACVD modified Dyneema® SB51 fibrous material with HMDSO showed unregularly deposited particles of SiO_2 onto the surface.

◼ Conclusions

The development of a synthesis of plasma polymers with the PACVD method (Chemical Vapour Deposition) was planned within the research, as well as the deposition of polymers on aramid fibrous substrates (woven fabrics of p-aramid fibres) and UHMWPE (fibrous sheets of UHMWPE fibres). Selection of the type of plasma polymer deposited on substrates was made in terms of giving
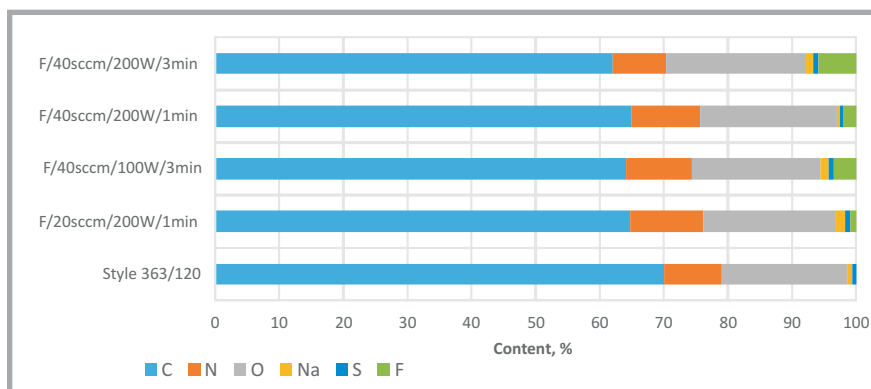
Figure 10. *Dependence of the surface composition of p-aramid woven fabric Style 363/120 on the parameters of the modification process with low-temperature plasma in the presence of TDFH vapours.*
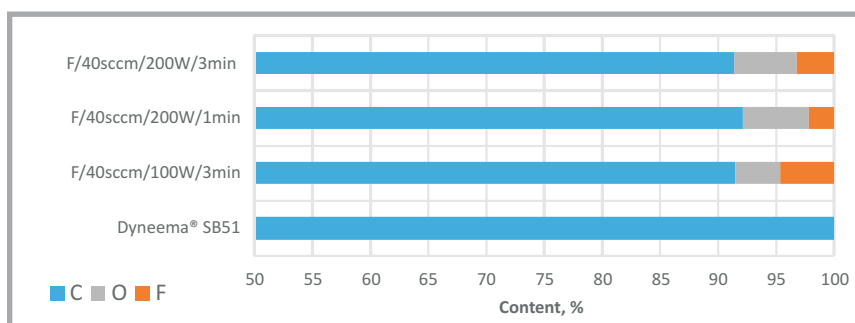
Figure 11. *Dependence of the composition of the surface of fibrous sheets of Dyneema® SB51 material on the parameters of the modification process with low-temperature plasma in the presence of TDFH vapours.*
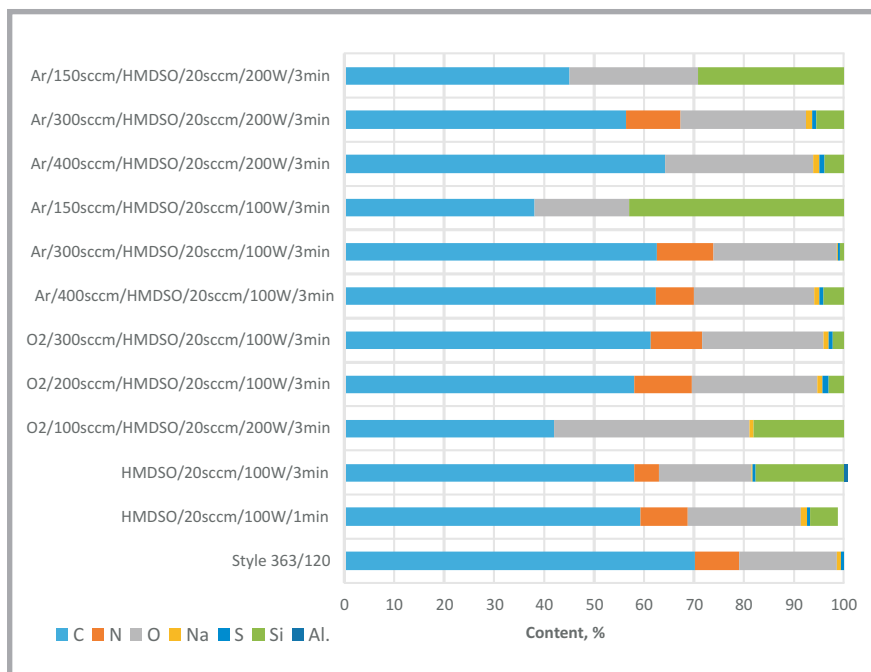
Figure 12. *Dependence of the composition of the surface of p-aramid Style 363/120 woven fabric on the parameters of the modification process with low-temperature plasma.*

the substrates specific surface properties: barrier, hydrophobic and tribological. Also synthesis was planned for two kinds of polymer: based on the vapours of organofluorine (Tetradecafluorohex-

ane) and organosilane (Hexamethyldisiloxane) monomers.

Moreover, at the initial stage of research, performing the activation was presumed
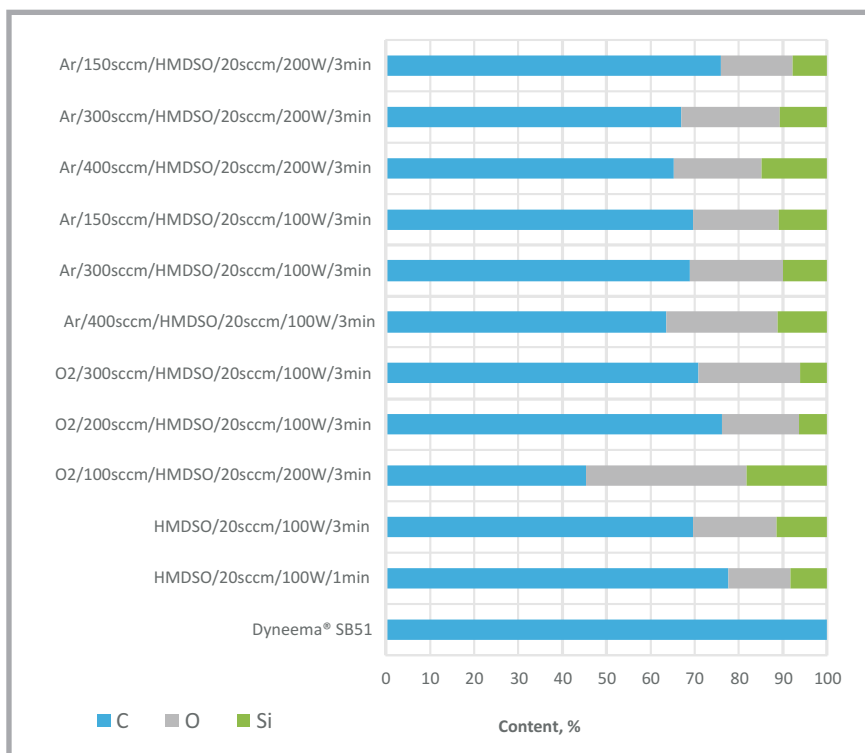
Figure 13. *Dependence of the surface composition of Dyneema® SB51 fibrous material on the parameters of the low-temperature plasma modification process.*
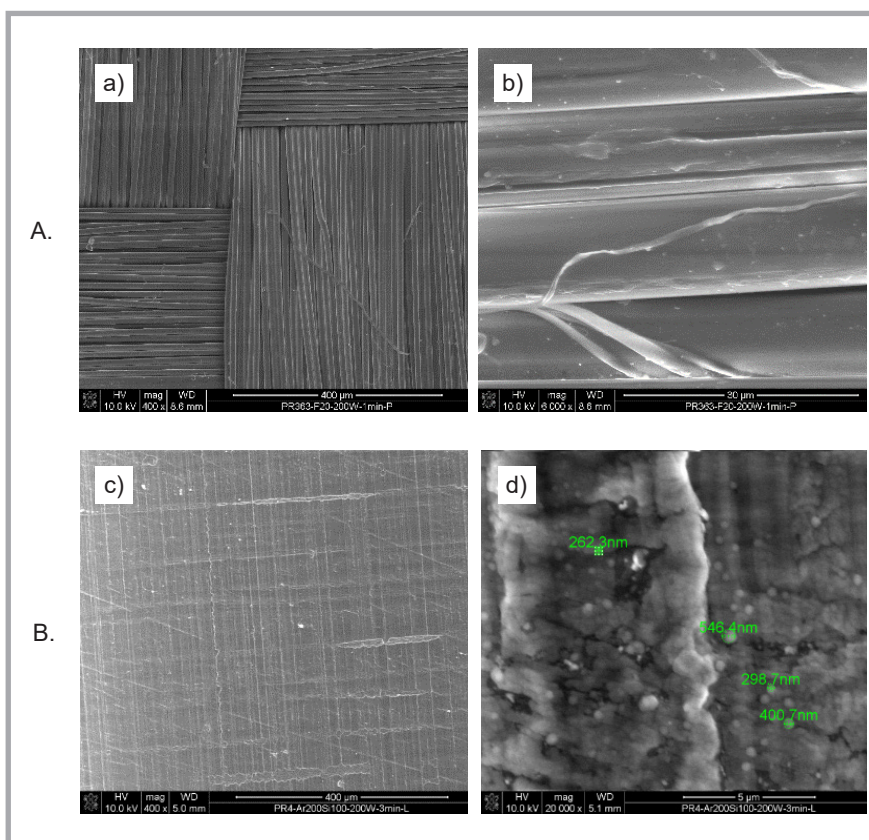

Figure 14. *Microphotographs of the PACVD modified structures: A) p-aramid woven fabric (polymerisation in a stream of tetradecafluorohexane at a the flow rate of: 0.032 - 0.064 Pa m³ s⁻¹ with power applied to the electrodes of 100 – 200 W, in a time period of 1 - 3 min); B) Dyneema® SB51 fibrous material (polymerisation of HMDSO at a flow rate of 0.032 Pa m³ s⁻¹, in a stream of process gas Ar at a flow rate of 150 - 0.48 Pa m³ s⁻¹, with power applied to the electrodes of 100 W, in time period up to 3 min); Mag.: a) 400×, b) 6000×, c) 400×, d) 20000×.*

for the substrate' surfaces in the environment of low-temperature plasma with the use of various process gases. The surface activation of the substrates ensured proper adhesion of the coatings created to the substrates.

Detailed conditions of low-temperature plasma modification in the presence of vapours of HDMSO or THDF were defined for two textile media. Organofluorine coatings were made under varied conditions of processing (the flow rate of monomer vapours, power applied to the electrodes, time period of plasma interaction with the substrate i.a.). Also organosilane coatings were made under varied conditions of processing (three kinds of carrier gases, the flow rate of monomer vapours and auxiliary gases, power applied to the electrodes, time period of plasma interaction with the substrate). The variants of textile materials made under diverse conditions were assessed for the effectiveness of modification based on ATR-FTIR and SEM-EDX research.

On the basis of the analysis results, the conclusion was drawn that it is possible with the plasma jet system to obtain coatings which are hydrophobic, free of defects and featuring the planned rate of deposition of the organofluorine compound onto the substrates: p-aramid Style 363/120 woven fabric as well as a fibrous sheet of Dyneema® SB51 material of UHMWPE fibres, adopting the process conditions as follows:

- polymerisation in a stream of tetradecafluorohexane at a flow rate of: 0.032 - 0.064 Pa m³ s⁻¹ with a power applied to the electrodes of 100 – 200 W, in the time period of 1 - 3 min.

It is also possible with the plasma jet system to obtain coatings which are hydrophobic, free of defects and comprising structures similar in terms of composition to SiO_2, by adopting the process conditions as follows:

- for Style 363/120 woven fabrics: the polymerisation of HMDSO 0.032 Pa m³ s⁻¹ in a stream of process gas Ar at a flow rate of 0.24 Pa m³ s⁻¹, with a power applied to the electrodes of 100 W, in a time period up to 3 min.
- for the fibrous sheet of Dyneema® SB51 of UHMWPE fibres: polymerisation of HMDSO at a flow rate of0.032 Pa m³ s⁻¹, in a stream of process gas Ar at a flow rate of 150 - 0.48 Pa m³ s⁻¹, with a power applied to the electrodes of 100 W, in a time period up to 3 min.

The modification of ballistic textiles with the use of PACVD technique as elaborated in this study is a promising technology for the performance and safety improvement of ballistic body protectors, such as ballistic vests as an example. The safety increase is not at least the result of the significant increase of the stability of the surface structures obtained.

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