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# Structural Changes in Plasma Assisted Chemical Vapour Deposition-Modified Ultra-high Molecular Weight Polyethylene, Ballistic Textiles During Accelerated Ageing

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## Abstract

The aim of this study was to compare the susceptibility of the plasma assisted chemical vapour deposition (PACVD) - surface modification of ultra-high molecular weight polyethylene (UHMWPE) fibrous composite to conditions of use and storing simulated by accelerated aging. Aspects of heksametylodisiloksan (HMDSO) implementation as donor for deposited during PACVD modification nanolayer as well as the selection of a new textile carrier were discussed. For the identification of potential changes in PACVD - modified UHMWPE, with the Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS) techniques were applied. The PACVD surface modification of UHMWPE showed insignificant changes in structural properties after using temperature or simultaneously temperature and humidity ageing factors. The process of accelerated ageing confirmed the time-stable presence of silicon contained in the polymer layer in both cases: when temperature or simultaneously temperature and humidity were used as accelerated aging factors. No significant changes in the morphology nor topography of the fibrous materials tested were found, subjected or not to the process of PACVD - modification using the HMDSO as a substrate for the surface-deposited polymer.

**Key words:** chemical modification, surface modification, PACVD, composites, material properties, material strength, soft UHMWPE fibrous composite.

## Introduction

The most important problem of ballistic materials is to maintain properties related to the safety and performance of ballistic protectors during long term use in various, somehow changed, conditions [1 - 3].

The ultra-high molecular weight polyethylene (UHMWPE) fibrous composite is one of the materials most often applied for the manufacture of ballistic inserts for personal body armour, which is based on fibres produced using the proprietary gel spinning process [4 - 5].

The soft UHMWPE fibrous composite offers maximum strength combined with minimum weight. It is characterized by 1500% higher strength than quality steel and up to 40% than aramid fibres [6, 7].

The time-stable functionalities of ballistic textiles during the storage and use of ballistic products provides an essential correlation 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 - 3].

Increasing the functionality or establishing new targeted properties with Plasma Assisted Chemical Vapour Deposition

(PACVD) allows for forming nanolayers, thereby creating new functional groups while minimizing thermal degradation processes and obtaining a relatively rapid and sustained result [8 - 12].

In [1, 6] studies on the surface modification of para-aramid ballistic woven fabrics using Plasma Assisted Chemical Vapour Deposition (PACVD) were described. The stability of the structural properties of PACVD-modified p-aramid textiles during accelerated ageing using temperature or simultaneously temperature and humidity as accelerated factors was studied in detail and compared with unmodified woven fabrics.

In summary, it should be noted that the publications available including [1] focus only on the modification of simple material systems – fibres made of polyethylene or para-aramid.

PACVD modification of the UHMWPE fibrous composite with deposition of a silicon containing polymer layer carried out in a strictly defined process should be ensure the functionality of the ballistic material during use, transportation and storing. This sentence constitutes the main research thesis.

The aim of this study was to compare the susceptibility of the PACVD-modified UHMWPE fibrous composite the accelerated aging, in which the standard conditions of use with a native composite were simulated. Aspects of the heksametylodisiloksan (HMDSO) used for deposition during PACVD modification of the nanolayer were discussed.

## Materials

### Textile materials

The Dyneema® SB51 UHMWPE fibrous composite (DSM, The Netherlands) was

**Table 1.** Specification of the Dyneema® SB51 fibrous composite [1, 4, 6].

Surface density, g/m <sup>2</sup>	Thickness, mm	Tensile strength, N		Elongation at the maximum force, %		Bursting strength, N
		Longitudinal	Vertical	Longitudinal	Vertical	
PN-ISO 2286-2:1999	PN-ISO 2286-3:2000	PN-EN ISO 1 421:2001				PN-EN 863:1999
251 ± 2	0.19 ± 0.02	9047 ± 880	7850 ± 1020	4.3	4.1	182 ± 8

used during the study. The soft ballistic Dyneema® composite consists of UHMWPE fibres (70 wt%) as the main compound with the addition (30 wt%) of low molecular weight polyethylene (LMWPE) and polyisoprene binder matrix [13, 15].

The main properties of Dyneema® SB51 are presented in *Table 1* (see page 63).

### Substrates for PACVD (Plasma Assisted Chemical Vapour Deposition)

Dyneema Dyneema® SB51 modification using the heksametylodisiloksan ( $C_6H_{18}OSi_2$ ; HMDSO) by Sigma Aldrich, USA.

## Methods

### Surface modification of Dyneema® SB51 by PACVD

The modification of Dyneema® SB51 in glow discharges was performed in a commercial plasma jet CD 400PLC ROLL CASSETTE (EUROPLASMA, Belgium) according to [14].

The PACVD-modified Dyneema® SB51 was made using the following processing parameters: polymerisation in a stream of HMDSO of flow:  $0.032 \text{ Pa m}^3 \text{ s}^{-1}$  with power applied to the electrodes of 100 W, for a time of 3 min.

### Accelerated ageing

The process of accelerated ageing of the modified and unmodified materials was carried out according to [14].

### Analytical methods

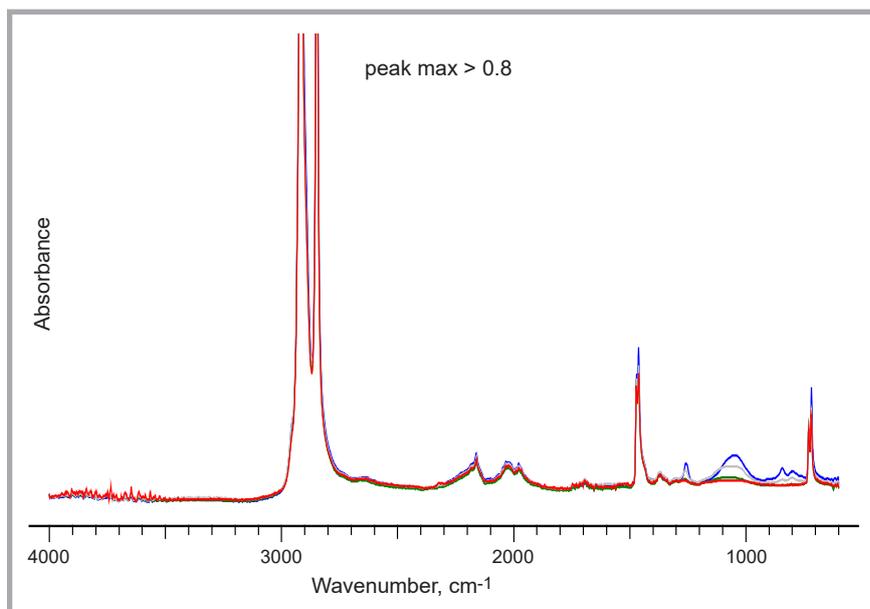
#### ATR-FTIR

An FTIR study was performed with a Nicolet 6700 iS10 spectrophotometer from Thermo Scientific, with the Attenuated Total Reflection (ATR) reflection technique, within the range of  $4000 - 464 \text{ cm}^{-1}$ .

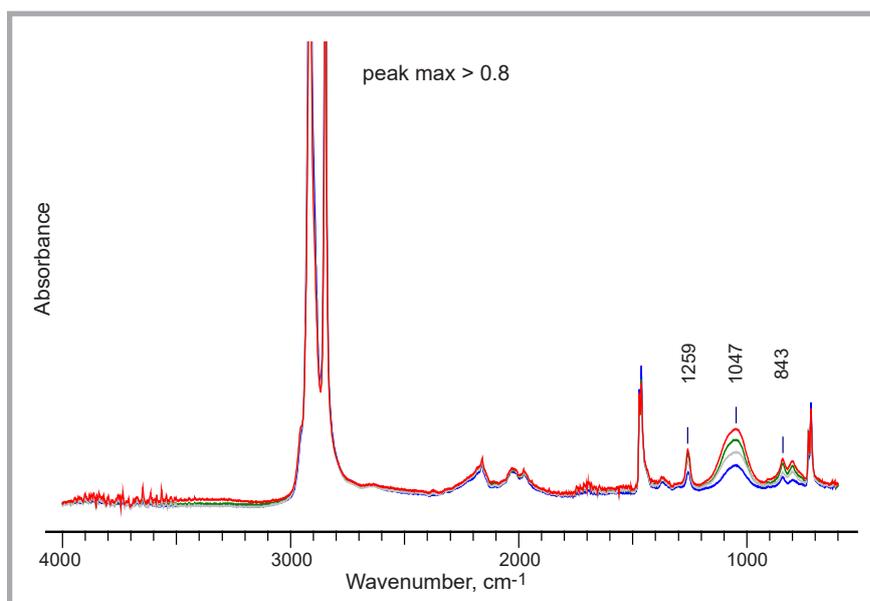
The tests were performed according to the method described in [1].

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

Chemical and morphological analyses 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 an X-ray microanalyser EDS (Energy-dispersive X-ray Spectroscopy)



**Figure 1.** ATR-FTIR spectra of the unmodified Dyneema® SB51 fibrous composite before and after the process of accelerated ageing with temperature: --- initial, --- after 28 days of accelerated ageing, --- after 35 days of accelerated ageing and, --- after 42 days of accelerated ageing.



**Figure 2.** ATR-FTIR spectra of the PACVD-modified Dyneema® SB51 fibrous composite before and after the process of accelerated ageing with temperature: --- initial, --- after 28 days of accelerated ageing, --- after 35 days of accelerated ageing and, --- after 42 days of accelerated ageing.

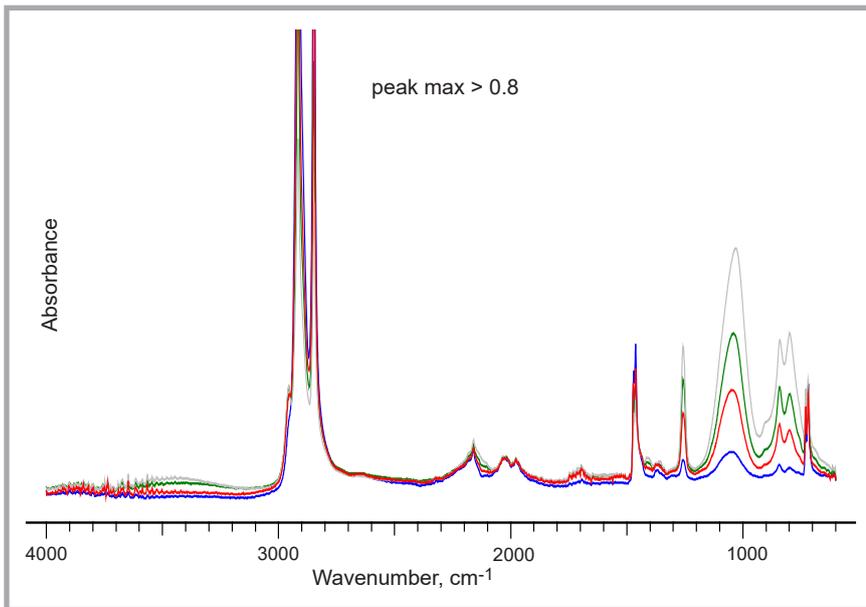
from EDAX (Detector SDD, energy resolution: Mn 132 eV) as described in [1].

## Results and discussion

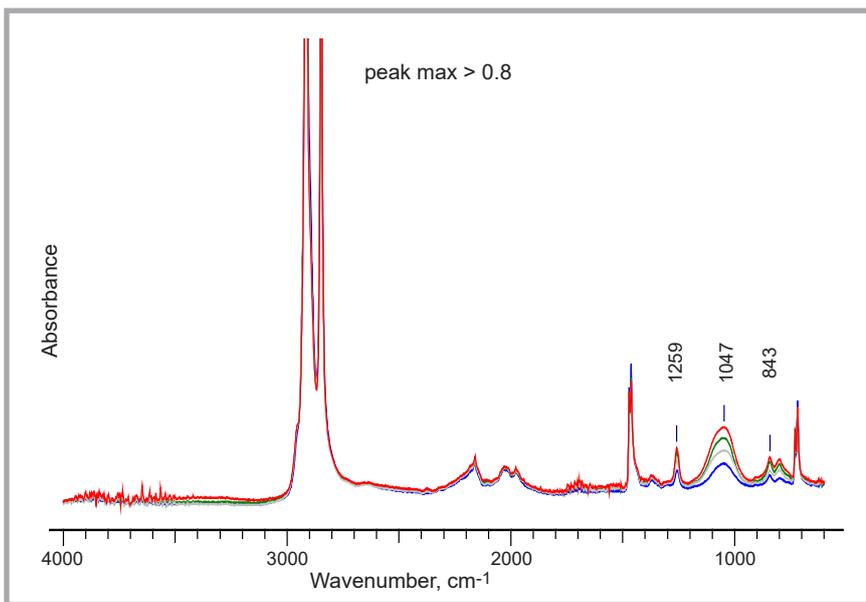
### ATR-FTIR analysis

ATR-FTIR spectra of the samples of unmodified fibrous composites subjected to the process of accelerated ageing with the temperature agent, compared with the ATR-FTIR spectrum of the initial Dyneema® SB51 are shown in *Figure 1*.

The process of the accelerated ageing of unmodified Dyneema® SB51 subjected to accelerated ageing using the temperature ageing factor did not cause significant changes in its ATR-FTIR spectra. The ATR-FTIR spectrum of the aged samples did not show a significant increase in the molecular structure compared to the initial material (non-aged). The condition of aging did not significantly affect the structural properties of the UHMWPE fibrous composite.



**Figure 3.** ATR-FTIR spectra of the unmodified Dyneema® SB51 fibrous composite before and after the process of accelerated ageing with temperature and humidity: --- initial, --- after 28 days of accelerated ageing, --- after 35 days of accelerated ageing and, --- after 42 days of accelerated ageing.



**Figure 4.** ATR-FTIR spectra of the PACVD-modified Dyneema® SB51 fibrous composite before and after the process of accelerated ageing with temperature and humidity: --- initial, --- after 28 days of accelerated ageing, --- after 35 days of accelerated ageing and, --- after 42 days of accelerated ageing.

ATR-FTIR spectra of the PACVD-modified Dyneema® SB51 fibrous composite subjected to accelerated ageing using the temperature ageing factor, compared to the initial PACVD-modified material are shown in **Figure 2**.

In the ATR-FTIR spectra of PACVD-modified Dyneema® SB51 before and after the accelerated aging process, absorption bands were observed at  $\lambda = 822 \text{ cm}^{-1}$  ( $-\text{Si}-\text{O}-\text{Si}$ ),  $\lambda = 1050 \text{ cm}^{-1} - 1047 \text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_2-\text{Si}$ ),  $\lambda = 1259 \text{ cm}^{-1} - 1252 \text{ cm}^{-1}$

( $\text{Si}-\text{CH}_3$ ) and  $\lambda = 2957 \text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_3$ ). The aging process did not show significant changes in the intensity or shift in the absorption bands characteristic of PACVD resulting from the silane polymer as compared to bands related to polyethylene, which confirms the implementation of new functional groups in UHMWPE resistant to the accelerated aging factor .

**Figure 3** shows ATR-FTIR spectra of the unmodified Dyneema® SB51 fibrous

composites before and after the process of accelerated ageing with simultaneous action of the temperature and humidity ageing factors.

Generally the process of accelerated ageing of unmodified Dyneema® SB51 with the simultaneous action of temperature and humidity ageing factors did not cause significant changes in the ATR-FTIR spectra, except a clear increase in the intensity of the absorption at wavenumbers of approx.  $\lambda = 1715 \text{ cm}^{-1}$  (caused by the oxidation of the low molecular weight polyethylene fraction). The phenomenon above possibly arises from the uniform coating surface of the UHMWPE composite by silane polymer, preventing the oxidation of the polyethylene matrix during accelerated aging. On the other hand, the ATR-FTIR spectra showed an increase in the absorption band intensity related to hexamethyldisiloxane moieties.

Implementation of the additional ageing factor - relatively high humidity caused the more dynamic oxidation of the low molecular weight (LMW) PE fraction as compared with the sample aged using the temperature ageing factor only.

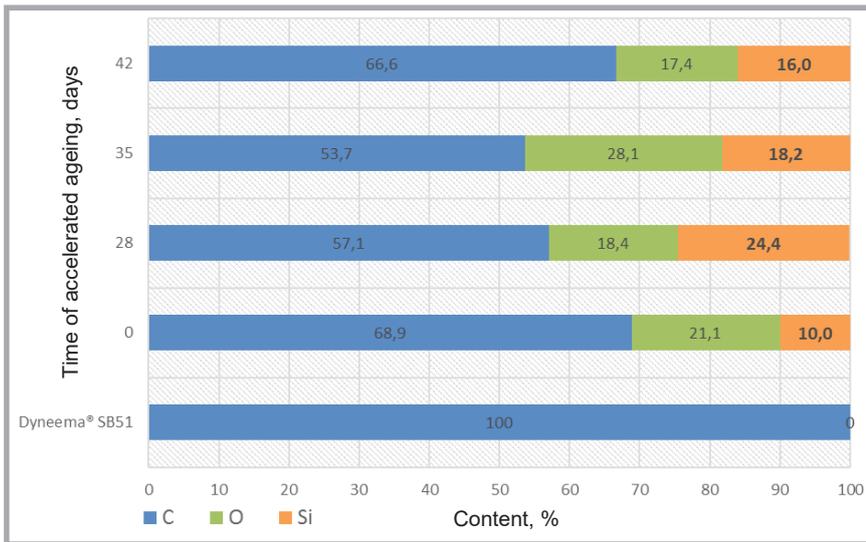
ATR-FTIR spectra of the PACVD-modified Dyneema® SB51 fibrous composite before and after the process of accelerated ageing with the simultaneous action of temperature and humidity are shown in **Figure 4**.

The ATR-FTIR spectra of the PACVD-modified Dyneema® SB51 fibrous composite before and after the accelerated ageing process are characterized by the presence of the following absorption bands at wavelengths  $\lambda = 822 \text{ cm}^{-1}$  ( $-\text{Si}-\text{O}-\text{Si}$ ),  $\lambda = 1050 \text{ cm}^{-1} - 1047 \text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_2-\text{Si}$ ),  $\lambda = 1259 \text{ cm}^{-1} - 1252 \text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_3$ ) and  $\lambda = 2957 \text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_3$ ).

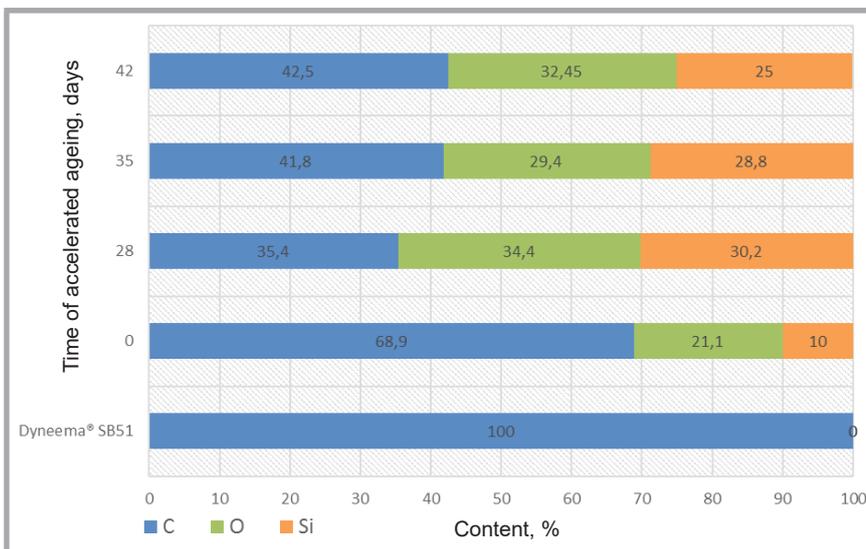
The accelerated aging process did not influence the intensity of absorption bands related to the silane polymer in contrast to the bands resulting from the polyethylene. A similar phenomenon was observed for aging using the temperature aging factor in the intensity of the band resulting from the oxidation of the LMWPE fraction.

#### The SEM-EDS analysis

The elementary composition of the PACVD-modified composite surface



**Figure 5.** Surface composition in % of the initial PACVD-modified Dyneema® SB51 fibrous composite, and those subjected to the accelerated ageing process with temperature.



**Figure 6.** Surface composition in % of the initial, PACVD-modified Dyneema® SB51 fibrous composite, and those subjected to the accelerated ageing process with temperature and humidity.

after accelerated ageing with temperature as the ageing factor is shown in **Figure 5**.

In the first stage of the accelerated ageing process (after 28 days) a significant increase (from approx. 10% to approx. 24%) in the silicon content may be due to the smoothing of the surface of PACVD-modified sample as result of the conditions of accelerated aging. The prolongation of accelerated aging caused a slight decrease in silicon content on the PACVD-modified surface (from approx. 24% to approx. 18% and 16%).

Changes in the surface elementary compositions of the PACVD-modified Dyneema®/SB51 fibrous composite sub-

jected to accelerated ageing with temperature and humidity are shown in **Figure 6**.

The process of accelerated aging of PACVD-modified composites carried out with temperature and humidity caused a similar alteration in the elementary surface composition to that for accelerated ageing with temperature. The first period of accelerated aging affected an increase in silicon content of up to 34% rather than a reduction as with the prolongation of accelerated aging. The phenomenon above is probably connected with the synergistic effect of the degradation of low molecular polyolefin and smoothing of the surface of the fibrous compos-

ite during the accelerated aging, resulting in a quasi-passive migration effect of plasma processing silane-like-polymer onto the surface on the newly-formed layer.

## Summary

In the research a wide range of verifications were carried out within the range of possible structural changes during the accelerated ageing process occurring in the (plasma-formed silane polymer) layer deposited by the PACVD process onto the Dyneema® SB51 fibrous composite. The test results were compared with the unmodified samples, the initial ones and after those accelerated ageing.

The accelerated ageing of the PACVD-modified UHMWPE fibrous composite with the subsequent deposition of silicon-containing polymer results in an increase in the amount of silicon on the surface of the composite. The phenomena observed is probably related to the partial, low-particle degradation, smoothing of the surface and the quasi migration of silicon onto the composite surface, allowing for better detection with the EDS and ATR-FTIR methods.

## Conclusions

Structural changes occurring in the fibrous composite materials subjected and not to the process of PACVD in the presence of organic silicon substrates under the impact of the accelerated ageing process were directly determined by the ageing factors applied.

The process of accelerated ageing confirmed the time-stable presence of the silicon containing polymer layer in both cases when temperature or simultaneously temperature and humidity were used as the accelerated aging factors.

No significant changes in the morphology nor topography of the fibrous materials tested were found, subjected or not to the process of PACVD-modification using the HMDSO as a substrate for the surface-deposited polymer.

As a result of the study, the relatively high resistance of the silicon-containing polymer in the PACVD-deposited layer was confirmed, irrespective of the conditions of accelerated ageing.

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