USING OF DSCBD PLASMA FOR TREATMENT OF KEVLAR AND NOMEX FIBERS

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Introduction

Aramids are a family of nylons, including Nomex and Kevlar. Chemical structure of Nomex and Kevlar fibers can be described by the common formula in Fig. 1 a 2.

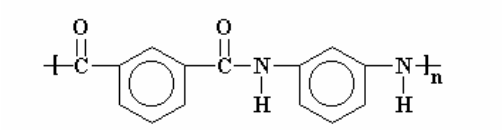

Fig. 1. **Structure of Nomex fiber**

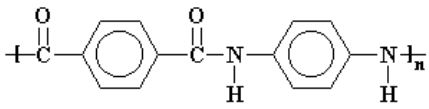

Fig. 2. **Structure of Kevlar fiber**

In Kevlar the aromatic groups are all linked into the backbone chain through the 1 and 4 positions (called para-linkage). Kevlar has high strength, high modulus (stiffness), toughness and thermal stability. Also it is resistant to many of the chemicals and solvents. It has high physical resistance, like high break and tear resistance and also presents high durability through for example high abrasion resistance.

Nomex has meta-phenyle groups, that is the amide groups are attached to the phenyl ring at the 1 and 3 positions. Nomex is inherently flame resistant and presents a high resistance to chemicals and does not dissolve easily, but is prone to hydrolysis. One way to prevent hydrolysis is using a diffusion barrier discharge[1]. After this treatment, Nomex fiber is absolutely resistant to 85 % H_2SO_4.

Their applications are focused on the technical sphere. They are usually used in tyre reinforcement, ballistics applications, ropes and cables, and in protective apparel where high strength, and thermal, puncture, and cut resistance are required[2].

For some applications it is necessary to improve surface properties. One of possible way is plasma treatment – subject of this study.

Plasma treatment is probably the most versatile surface treatment technique. Different types of gases (argon, oxygen, nitrogen) can produce the unique surface properties required by various applications. The advantage of plasma treatment is the fact that plasma treatment usually changes surface properties of polymers without interfering the bulk properties[3].

To modify polymer surface it is possible to employ oxygen or nitrogen-containing plasma. A variety of oxygen functional groups (e.g. C–O, C=O, O–C=O, C–O–O) we can obtain from oxygen-containing plasma. Due to plasma treatment it can be improve wettability, printability and biocompatibility of polymer surfaces[3].

Experimental

Materials

The fibers used in this experiment were Kevlar and Nomex. Before plasma treatment, all fibers were washed twice with isopropyl alcohol for 2 min and dried in oven at 50 °C for 1 hour. Than samples were let in a fume chamber for 24 hours.

Plasma treatment

An atmospheric pressure plasma source of Diffuse Coplanar Surface Barrier Discharge (DCSBD) was employed for the plasma treatment of samples. To initiate plasma, atmospheric air and nitrogen were chosen as working gases. Model of used equipment is DSCBD A4-LIN (Fig. 3), which means that is device with linear displace. The discharge power was 300 W and frequency 15 kHz. Fibers of Kevlar and Nomex were treated by plasma for 30 sec, 2 and 5 min.

SEM morphological study

Surface morphology of fibers was investigated using scanning electron microscopy (SEM). It was performed in TS5130 VEGA TESCAN at magnification of $1.5 \cdot 10^5$ and

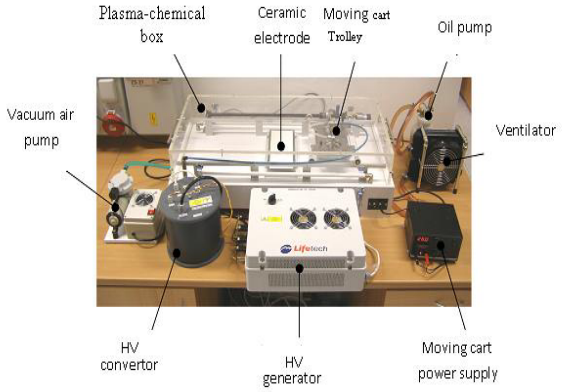

Fig. 3. **The photo of plasma source of DCSBD**

a voltage of 30 kV.

Before SEM analysis, all the samples were coated by platinum with model of PRONEN SCD 030. Conditions of coating were 120 s, electric current 115 mA at vacuum.

FTIR analysis

A FTIR spectrophotometer (model One, Perkin Elmer – ATR technique on ZnSe crystals) was used to analyze the functional groups of the surface pure and plasma treated fibers. Thickness of analysed surface layer is in the micron range.

XPS surface chemical analysis

The X-ray photoelectron spectroscopy (XPS) experiment was performed using ESCA PROBE P photoelectron spectrometer (Omicron Nanotechnology Ltd) equipped with Al anode (1486,7 eV) X-ray source. The base pressure in the sample chamber was controlled in the range of 10^{-10} mbar. Thickness of analysed surface layer is in the range from 5 to 10 nm.

Measured spectra were analysed by way of CasaXPS programme. Deconvolution analysis of the C1s peaks was performed to determine changes of functional groups.

Results and discussion

SEM results

Fig. 4a-d show the SEM micrographs of untreated and plasma-treated Kevlar fibers. It can be observed that no ripple-like structure has been shown on fibers after the plasma treatment neither in the air nor nitrogen.

Some irregularities on Nomex fiber can be proceed from manufacturing process. After air-plasma or nitrogen plasma treatment, no ripple-like structures can be obtained as shown Fig. 5a-c. Plasma treated Nomex fiber has a rougher surface than untreated fiber.

On these fibers the etching action of ions is weaker than on other polymers. It is due to high crystallinity of fibers and rigidity of polymer chains.

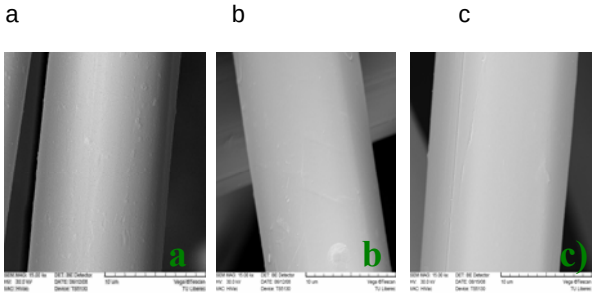

Fig. 4. **SEM micrographs of Kevlar fiber:** a) untreated, b) air-plasma treated after 5 min, c) nitrogen-plasma treated after 5 min

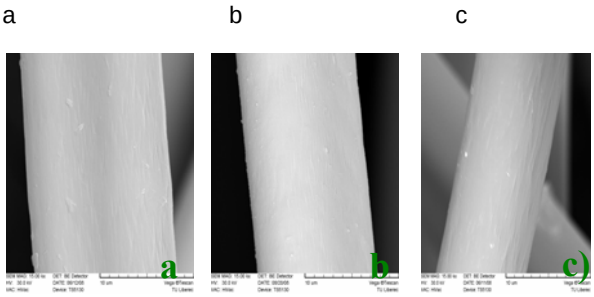

Fig. 5. **SEM micrographs of Nomex fiber:** a) untreated, b) air-plasma treated after 5 min, c) nitrogen-plasma treated after 5 min

FTIR analysis

No significant changes in IR spectra of Kevlar fibers were observed for air-plasma and nitrogen-plasma treatment (Fig. 6, 7).

We can observe on slight changes in IR spectra of Nomex fiber after plasma treatment (Fig. 8, 9). These changes were found in C=O groups at 1740 cm^{-1} and O=C–O– groups at 1124 cm^{-1}.

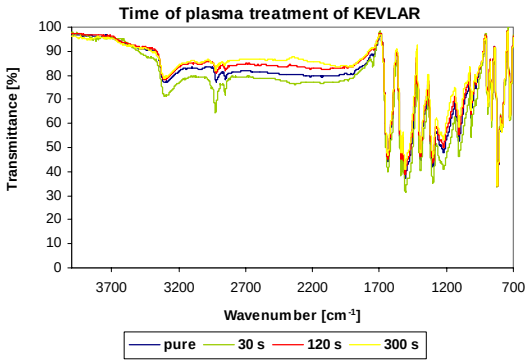

Fig. 6. **FTIR spectra of Kevlar fiber after air-plasma**

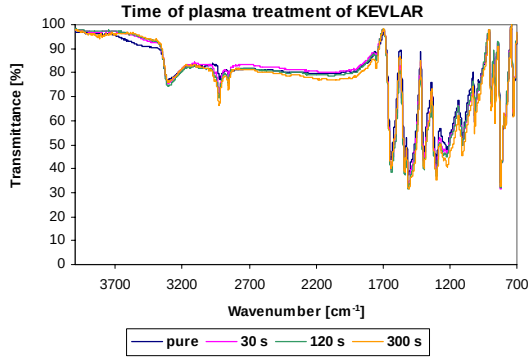

Fig. 7. **FTIR spectra of Kevlar fiber after nitrogen-plasma**

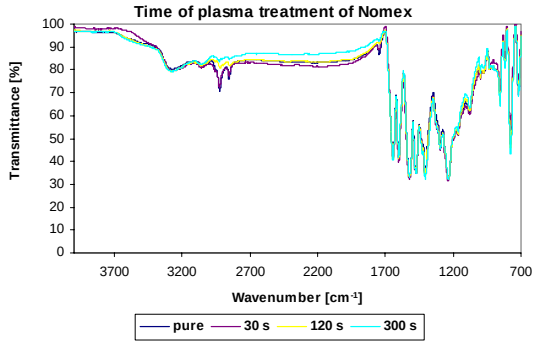

Fig. 8. **FTIR spectra of Nomex fiber after air-plasma**

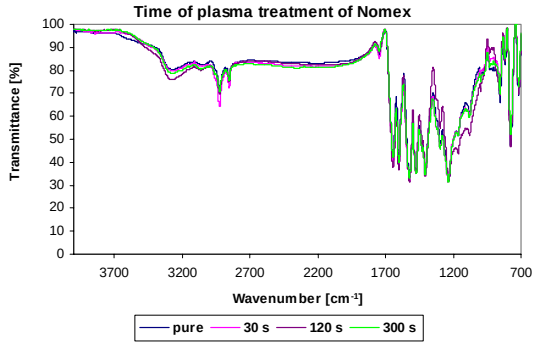

Fig. 9. **FTIR spectra of Nomex fiber after nitrogen-plasma**

XPS results

XPS analysis was performed to estimate changes in chemical composition of the fiber surfaces. For chemical analysis, where carbon bonds are determined by virtue of curve-fitted spectra, we used these values of carbon energy C 1s obtained on account of literary references[4–6]. The aramid fiber surface after plasma treatments has potential carbon-containg components with binding energies of 284,7 eV (C–C), 2863 eV (C–O/C–N), 287,5 eV (C=O), 289 eV (C=OOH).

Obtained results are summarized in Tab. I and II. After plasma treatment, the concentrations of oxygen significantly increased for all plasma treated samples. Also we can see a significant reduction in concentration of carbon. It is a typical effect for plasma treated polymers[7]. It is caused by the active species in plasma due to the chain scission mechanisms.

We can conclude that the air-plasma and nitrogen plasma treatment of fibers of Kevlar and Nomex leads to changes in chemical states of carbon and oxygen.

In order to examine changes of functional groups deconvolution analysis of the C1s peaks was performed (tab. III, IV). We can find that ketone groups concentration at Kevlar and Nomex fibers surfaces increased for almost all samples after plasma treatment.

Table I
Relative chemical composition and atomic ratios determined by XPS for fiber of Kevlar and Nomex after air-plasma treatment

Condition	Chemical composition [%]			Atomic ratio [%]	
Kevlar	C1s	O1s	N1s	O/C	N/C
untreated	81,29	13,69	5,02	16,84	6,18
plasma – 30 s	72,20	23,71	4,09	32,84	5,66
plasma – 120 s	71,25	22,89	5,85	32,13	8,21
plasma – 300 s	71,31	24,55	4,15	34,43	5,82
Nomex	C1s	O1s	N1s	O/C	N/C
untreated	79,25	14,74	5,22	18,60	6,59
plasma – 30 s	71,21	22,87	4,36	32,12	6,12
plasma – 120 s	66,23	27,61	6,15	41,69	9,29
plasma – 300 s	66,46	27,41	5,01	41,24	7,54

Table II
Relative chemical composition and atomic ratios determined by XPS for fibers Kevlar and Nomex after nitrogen-plasma treatment

Condition	Chemical composition [%]			Atomic ratio [%]	
Kevlar	C1s	O1s	N1s	O/C	N/C
untreated	81,29	13,69	5,02	16,84	6,18
plasma – 30 s	79,34	15,76	4,90	19,86	6,18
plasma – 120 s	74,75	20,20	5,04	27,02	6,74
plasma – 300 s	72,10	21,69	6,21	30,08	8,61
Nomex	C1s	O1s	N1s	O/C	N/C
untreated	79,25	14,74	5,22	18,60	6,59
plasma – 30 s	80,02	15,05	4,93	19,37	6,16
plasma – 120 s	75,72	17,23	7,06	22,75	9,32
plasma – 300 s	73,75	18,40	7,13	24,95	9,67

Table III
Results of analysis of C1s peaks for fibers of Kevlar and Nomex after air-plasma treatment

Condition	Relative area corresponding to different chemical bonds [%]			
Kevlar	C-C,H	C=O	C-O-	C=OOH
untreated	74,92	7,46	15,37	2,26
plasma – 30 s	75,44	12,12	12,44	–
plasma – 120 s	74,37	9,76	15,86	–
plasma – 300 s	78,19	12,70	9,11	–
Nomex	C-C,H	C=O	C-O-	C=OOH
untreated	85,36	6,52	8,12	–
plasma – 30 s	77,76	9,71	12,53	–
plasma – 120 s	70,64	11,39	12,71	5,26
plasma – 300 s	67,25	14,78	15,35	2,63

Table IV
Results of analysis of C1s peaks for fibers of Kevlar and Nomex after nitrogen-plasma treatment

Condition	Relative area corresponding to different chemical bonds [%]			
Kevlar	C-C,H	C=O	C-O-	C=OOH
untreated	74,92	7,46	15,37	2,26
plasma – 30 s	83,81	5,25	10,94	–
plasma – 120 s	85,19	3,63	11,18	–
plasma – 300 s	84,97	5,08	9,95	–
Nomex	C-C,H	C=O	C-O-	C=OOH
untreated	85,36	6,52	8,12	–
plasma – 30 s	76,57	4,64	18,83	–
plasma – 120 s	82,59	9,23	8,18	–
plasma – 300 s	79,13	6,51	14,36	–

Carboxyl groups of Kevlar fiber disappear after air-plasma and nitrogen plasma. It was found that content of carboxyl groups of Nomex fiber increased after longer times of plasma treatment in the air.

Conclusion

There are presented results of surface properties of Kevlar and Nomex fibers before and after plasma treatment in the air and in nitrogen.

No ripple-like structure is formed on surface of fibers of Kevlar and Nomex due to weaker etching action of DCSBD plasma in comparison with rigidity of polymer chains on these fibers.

Plasma treatment causes changes in chemical state of carbon and oxygen. While content of carbon decrease, content of oxygen significantly increased after plasma treatment of fibers of Kevlar and Nomex. This oxidation process was realised only in the surface layers of fibers. According this theory changes of surface were estimated only by XPS.

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Using of DSCBD Plasma for Treatment of Kevlar and Nomex Fibers

In this study the influence of plasma treatment on fibers of Kevlar and Nomex is discussed. These fibers were treated by means of the plasma source of Diffuse Coplanar Surface Barrier Discharge (DCSBD) at different conditions. The change in chemical compositions of pure, air-plasma and nitrogen-plasma treated Nomex and Kevlar fibers were analyzed by means of X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The morphologies of surface of the pure and air-plasma and nitrogen-plasma treated Kevlar and nomex fibers were analyzed by means of scanning electron microscopy.