

# NANOVLÁKENÝ KOMPOZITNÍ MATERIÁL INTEGROJÍCÍ NANO/MIKROČÁSTICE MEZI VLÁKNA

## NANOFIBROUS COMPOSITE MATERIALS INTEGRATING NANO/MICRO PARTICLES BETWEEN THE FIBRES

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### Abstrakt

Článek se zabývá kontinuální inkorporací částic sorbentu pomocí ultrazvuku přímo *in situ* do nanovlákné matrice vyrobené procesem elektrického zvlákňování. Tato technologie je založena na použití bez jehlového způsobu elektrického zvlákňování. Současně kombinuje použití ultrazvuku pro dosažení lepší dispergace sub-mikronových částic nebo mikročástic, které jsou zachyceny mezi nanovláknem tvořící nosný materiál. Hlavní výhodou použití těchto dvou technologií současně je nezávislost částic a jejich začlenění do procesu elektrostatičkého zvlákňování. Částice sorbentu jsou drženy mezi vlákny a jejich povrch zůstává volný (není překryt polymerem). Díky aktivnímu povrchu částic sorbentu jsou zachovány všechny aktivní vlastnosti daného sorbentu. Tyto kompozitní materiály mohou být jednoduše děleny např. nůžkami, bez následného uvolnění částic z materiálu. Jsou uvedeny i výsledky elektronové mikroskopie nově koncipovaného nanokompozitního materiálu a jeho morfologické analýzy, jako je např. rozložení částic. Materiál byl použit jako sorbent bis(2-chlorethyl)sulfidu (yperitu) se sorpční dobou delší než 240 minut. Tento unikátní materiál byl vyvinut pro použití pro ochranu proti bojovým chemickým látkám. Materiál může být použit i pro další aplikace v závislosti na práškovém sorbentu, který je dispergován do nanovlákné vrstvy.

**Klíčová slova:** nanovláknem, nanokompozit, inkorporace částic, ochranný materiál

### Abstract

This article deals with the continual incorporation of sorbent particles by the ultrasonic dispersion *in situ* into a nanofibrous matrix produced by the electrospinning process. The new technology is based on the use of the needleless electrospinning method in combination with the ultrasound-enhanced dispersion of sub-micro or micro particles, which are deposited between nanofibers onto the support material. The main advantage of use these two technologies in time is the independence of particle-incorporation of the electrospinning process. The sorbent particles are held in between the fibers and they remain uncovered by polymer. Thanks to free surface of sorbent particles are maintained all their active properties. Such materials can be simply cut with scissors without the releasing particles. Further the authors present figures from the electron microscopy of the newly-designed nanocomposite material and its morphological analysis, such as the particle distribution. The material was used as a sorbent of bis(2-chlorethyl) sulfide (mustard gas) with a sorption time greater than 240 minutes. This unique material has been developed to be used for protection against chemical warfare agents; yet, it can be employed for several other applications depending on the powder material dispersed onto the nanofibrous layer.

**Key words:** *nanofibers, nanocomposite, particle-incorporation, protection material*

## 1 INTRODUCTION

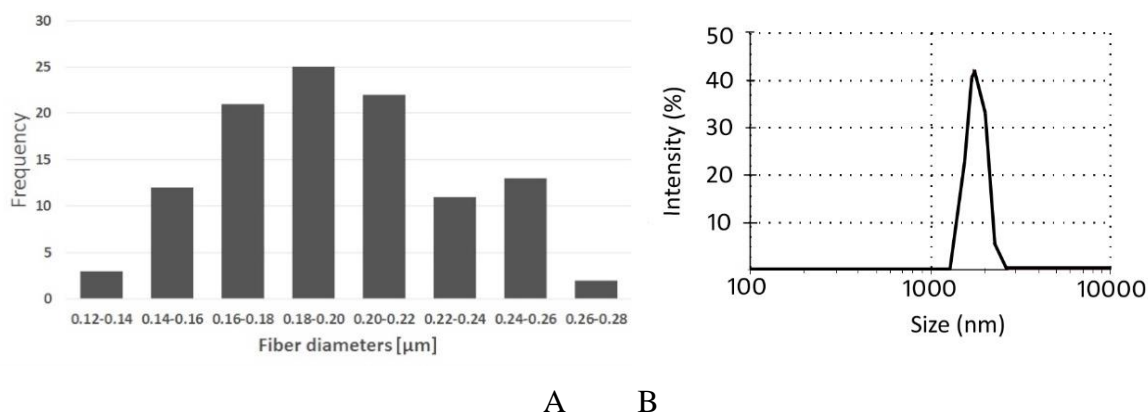
Nanofibrous materials can be produced by the many techniques which could be divided to two main groups the needle [1] and needleless [2,3] electrospinning processes. Composite materials consist of electro spun nanofibers are the new materials which could be further modified. There are several methods of modifications and we chose for that particles incorporation [4-10]. The nanofibrous composite materials, consist of the electrospinning nanofibers and dispersed particles. For that purpose, could be chose fullerenes [6], nanotubes [8,9], hydroxyapatite [7] or other sorbents. The particles could be incorporated from polymeric solutions, core-shell electrospinning [4,5] or a combination of the electrospinning and electro-spraying processes [10]. But all of these methods are limited, by the amount of the powder material. The viscosity of the polymeric solution increased by addition of any powder material, which has affect to the electrospinning process [6-9, 15].

The aim of this work was to developed a new type of sorbent material especially for sorption of mustard gas. The other applications, depends on the used powder as the sorbent. Further is introduced a new method for integration of particles in-between the nanofibers instead of into the fibres themselves. The particles in this experiment were dispersed by ultrasonic vibrations and then covered with the deposited nanofibers directly. The sorbent particles are stuck in-between the fibres, which allows a unique ultrasound incorporation. Thanks to these techniques could be achieved a higher density of particles on mass area density of composite material. In the chapter methods and materials is described the new-produced material, analysis and usage potential, as revealed by their tests for mustard gas penetration.

## 2 MATERIALS AND METHODS

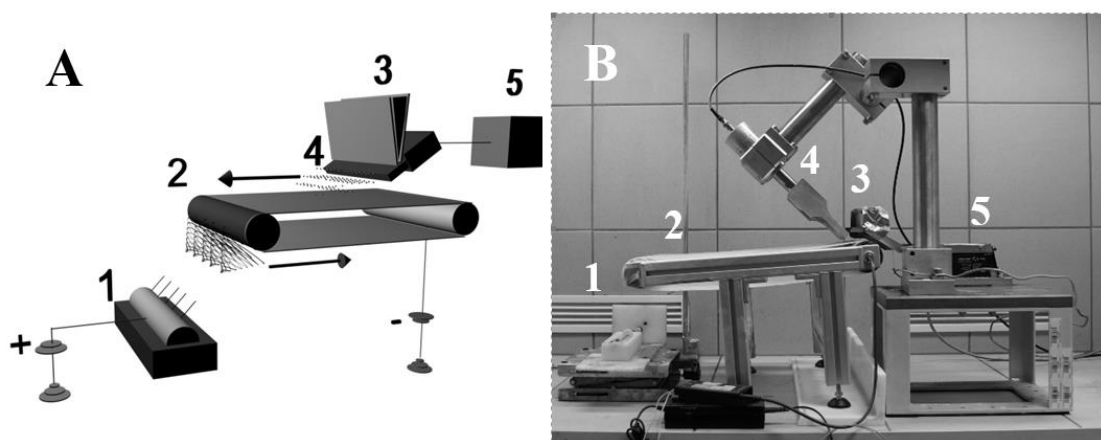
For the electrospinning process was used a 10wt% aqueous polyvinyl alcohol (PVA) solution was prepared by dissolving the PVA polymer in distilled water. The company Chemické závody, Nováky in Slovakia provided the PVA with a predominant molecular weight of 60.000 amu. Crosslinking of the PVA nanofibres was achieved by adding 3wt.% of 99% phosphoric acid and 4wt.% of Glyoxal, both of them were produced by Sigma Aldrich. The nanofibrous layer was then heated up to 135 °C for 5 minutes to activate the crosslinking process. Next, a polymeric solution for the electrospinning process was prepared from two components. Kuraray America, Inc. produced polyvinyl butyral (PVB), Mowital® B 60 H, with an average molecular weight of 60.000 amu; it was dissolved in a 10wt. % solution in ethanol–water (9:1 v/v).

The nanofibers were deposited on the polypropylene spunbond produced by Pegas Nonwovens, Czech Republic. The distribution of the fibre diameter lengths was in the range from 120 to 380 nm with an average of 200 nm. A histogram can be seen in *Figure 1A*, a size distribution in *Figure 1B*. The NIS Elements software produced by Nikon was used for calculations of the average inter-fibrous distance, which was identified as being  $(1.67 \pm 0.69) \mu\text{m}$ .



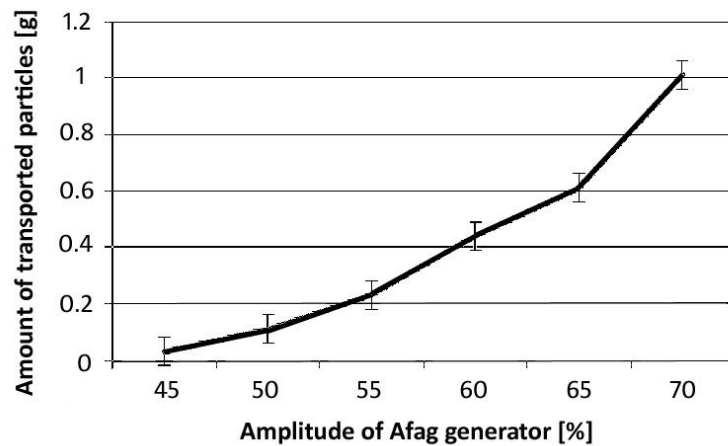
**Figure 1** A) The distribution of nanofibrous diameters measured by NIS element software and B) size distribution of the milled particles used for the ultrasonic spraying measured by the dynamic light scattering Zetasizer ZEN3601.

For the needleless electrospinning process the investigators used positive and negative high voltage sources, a 300 W, high voltage DC power supply with regulators, model number SL 150, manufactured by Spellman High Voltage, Inc. with output parameters of 0–50 kV, 6 mA. A schematic diagram and photography of the setup used are shown in Figures 2A and 2B, respectively. The positive voltage of 35 kV was applied to the roller (spinning electrode) and the negative voltage of 5 kV to the belt collector. The positive voltage was set to reach the critical voltage [2] and collector was negatively charged to increase the potential difference to support the collection of fibres preferentially to the belt collector. The distance between the spinner and the collector was kept at 15 cm which is the optimal distance for fibrous elongation and solvent evaporation. Nanofibers were collected on the belt collector, which consists of a motor powering two cylinders positioned 40 cm apart and holding the supported non-woven textile. The rotational speed of the gearbox powering the belt collector was 10 rpm and the belt was 80 cm long and 20 cm wide. First of all, simple nanofibrous layer without any particles was collected and then the belt collector was twisted three times while both electrospinning and ultrasonic dispersion processes were in progress [11,12]. Finally, the composite was covered by another additional nanofibrous layer. Both inner and outer nanofibrous layer was prepared for better manipulation with the material.



**Figure 2.** Schematic diagram (A) and photograph (B) of experimental setup for the creation of nanocomposite materials, which consists of (1) needleless spinning electrode, (2) belt collector, (3) particle conveyor, (4) ultrasound sonotrode, and (5) feeder.

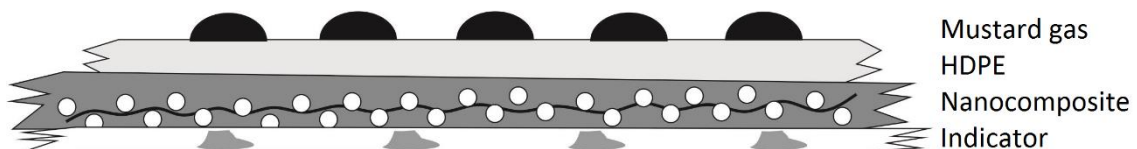
The particles were stored in a reservoir and continually conveyed by a series of vibrations to the edge of the sonotrode. The conveying device was specially designed for this technology. The device is powered by the Afag HLF 12 feeder controlled by the PSG1 unit with the vibrations amplitude with the constant frequency of 220 Hz. The relationship between the amplitude and the amount of the conveyed particles can be seen in Figure 3. The particles were subsequently covered by nanofibers. The temperature during the experiments was  $21 \pm 5$  °C and the relative humidity  $65 \pm 5$  %. A sieve shaker (Retsch AS 200) was used for testing the particles bonding to the fibres (*Fig. 3*).



*Figure 3.* The relationship between the amplitude and the amount of the conveyed particles.

### 3 ADSORPTION ABILITY OF THE NANOCOMPOSITE MEMBRANE

The nanofibrous material with incorporated particles of active carbon was tested for penetration of CWA. Ninety-six-per-cent-pure bis(2-chlorethyl) sulfide, or mustard gas was applied in the liquid phase on a membrane made of High Density Polyethylene (HDPE) with the thickness of 30  $\mu\text{m}$  [13]. The mustard gas vapor penetrating through the HDPE was adsorbed by the particles of active carbon. The sorption efficiency on the reverse side of the sample was evaluated by chemical indication factors caused by the degree of penetration and by gas chromatography. The chemical indication was based on the reaction of the penetrating mustard gas with a paper indicator saturated with chloramine (N-chlorobenzoic-o-toluidine) (*Fig. 4*). The change of the pH value was indicated by Congo red [13]. The gas chromatography used the flame-ionizing indication on a Carousel 2000 device to measure the mustard gas permeation [14]. The chemical sensitivity indication was 0.1  $\mu\text{g}$  of mustard gas.

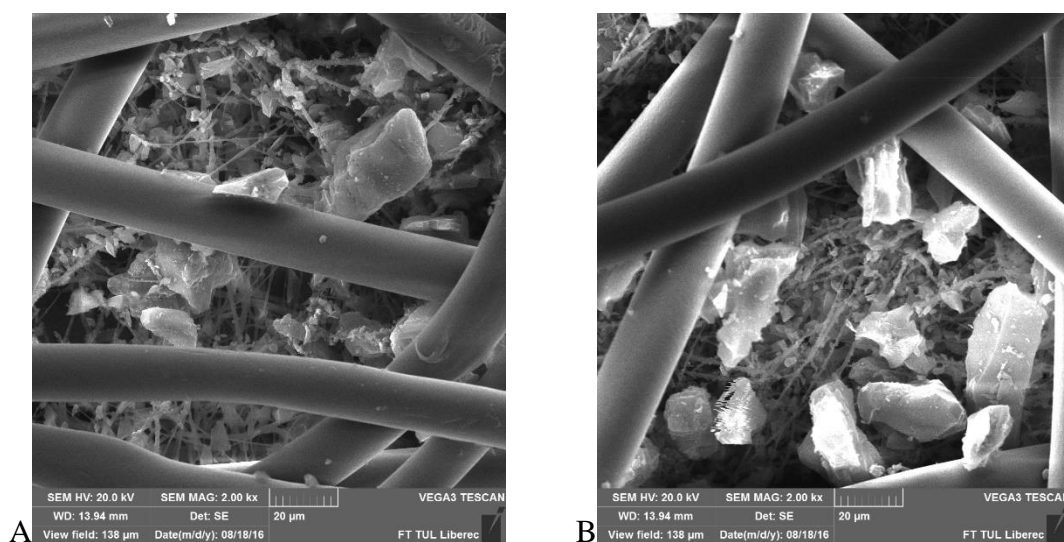


*Figure 4.* The setup for measuring the chemical indication of mustard gas (HD) where HDPE is the High Density Polyethylene membrane which covers the nanocomposite membrane with the indicator on its back.

## 4 RESULTS AND DISCUSSION

The formed nanofibrous composite material has unique properties due to its original and innovative structure. The particles are stuck in-between fibres and do not get covered by any polymer. The material can therefore keep its characteristics, such as, for example, high porosity in the case of active carbon particles.

The average areal density of the nanofibers was  $5 \text{ g.m}^{-2}$  and the areal density of particles reached up to  $20 \text{ g.m}^{-2}$  within 10 minutes. These values were measured independently for both processes by weighing the electro spun polymer and the dispersed particles. The amount of particles was controlled by the amplitude of the generator (see *Fig. 3*). The scanning electron microscope (SEM) images of the active carbon incorporated in-between the electro spun nanofibers and covered by spunbond are shown in *Figure 5A-B*.



**Figure 5A-B.** Scanning electron micrographs of electrospun nanofibrous material with particles of active carbon dispersed into the PVA nanofibrous layer and covered by spunbond.

From the SEM pictures in *Figure 5A-D* it is clearly seen that particles of active carbon have been trapped by the fibres. The nanofibrous web prevents their releasing even after it is cut, thus particles stay bonded to the layer. Some particles remained agglomerated due to the above mentioned reason. Samples used for SEM didn't have any additional covering nanofibrous layer for better observation of bonded particles.

## 5 CONCLUSION

The materials can be used for a number of technical applications. In the investigation they were successfully tested for the sorption of chemical substances, such as mustard gas. The direct action of the liquid mustard gas through the High Density Polyethylene gave high values of breakthrough time for the composites, but not for the membrane without sorbents. It is already possible to achieve such results with a relatively small amount of active carbon.

The technology developed in the investigation proved to be applicable for different powder materials. Its main advantage is the fact that the particles stay uncovered by the polymeric matrix and they keep their unique properties. They are simply trapped by the adhesion forces of the nanofibers, which enables the integration of even submicron particles depending

on the inter-fibrous porosity. It is as well possible to combine particle materials and electro spun polymers and to create a tailor-made product.

The composite material with particles was successfully tested for sorption of the mustard gas with time of sorption more than 300 minutes. However, some aspects of the material have to be improved, mainly the homogeneity of the dispersed material. This was evident for the active carbon particles. Active carbon is a very hygroscopic material and therefore its agglomeration increases during the process. The homogeneity can be improved, e.g. by use of some more closed system with air conditioning, which prevents the agglomeration of particles. Another possibility to improve the homogeneity of the particles distribution is the presence of some suction system under the nanofibrous layer.

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