HEALTH ASPECTS OF SILICON OXIDE NANOFIBERS

Jarmila Studničková[1], Lukáš Brázda[2], Aleš Helebrant[3], Petr Exnar[4]

Abstract: An important property of newly created materials which has to be tested is their effect on human organism. Lack of negative effects is one of the main conditions of their future successful use. The same applies to the inorganic silicon oxide nanofibers produced in the pilot plant by electrospinning of polymeric solution prepared by the sol-gel method. Because nanofibrous materials could be potentially dangerous if inhaled, the speed of their dissolution in simulated pulmonary fluid was experimentally observed. Comparison of observed results with published results of other inorganic fibrous materials shows that the speed of silicon oxide nanofiber dissolution is close to that of the HT Stonewool material which is considered safe.

1. Introduction

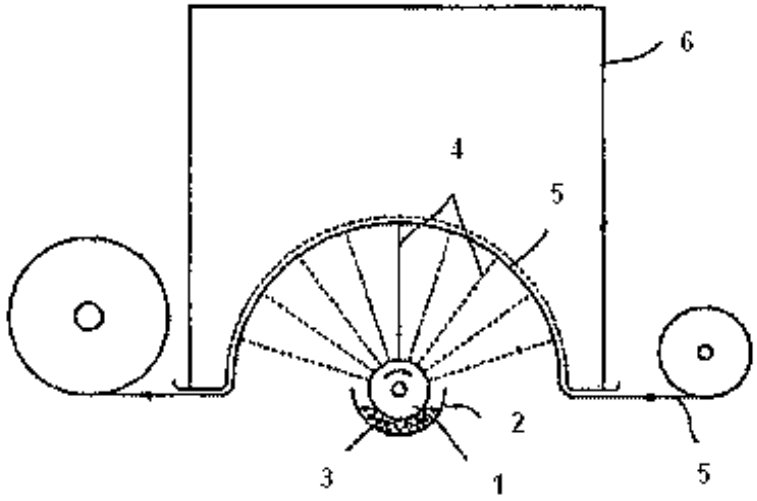
Under specific circumstances, inorganic fiber materials may cause cancer, especially in the case of thin fibers. These fibers can be inhaled and enter the lungs, while not being mechanically caught in the respiratory tract. The World Health Organization (WHO) stated that potentially carcinogenic fibers are fibers longer than 5 μm, less than 3 μm in diameter and with length/diameter ratio larger than 3. [1]

The fibers represent a danger to the human body when they show high biopersistence. This means they have a high ability to resist mechanisms of physiological degradation. The fibers in the human body can be dissolved directly in extracellular pulmonary fluid or degraded in a macrophages environment. In the case of dissolution, the toxicity of chemical fiber compounds is also important.

Nanofibrous materials are the phenomena of recent years. Generally, nanofibers are fibers with their diameters significantly less than 1000 nm. The Technical University of Liberec has found a way to mass produce nanofibers in its pilot plant. This finding has presented a lot of opportunities to utilize specific nanofiber properties, such as large specific surface area and high porosity or small pores between fibers in the nanofiber web. The principle of the patented device is shown in Figure 1.

The newly prepared group of nanofibers is a group of inorganic nanofibers, silicon oxide nanofibers in our case. It is also important to pay attention to the potential danger of tumour formation after nanofiber inhalation during its production or usage. The difference in chemical resistance (the speed of dissolution in lungs), is easily seen in the published pictures of fibers in rat lungs (Figure 2 and Figure 3).

[1] Ing. Jarmila Studničková, Technical University of Liberec, Department of Textile Chemistry, Faculty of Textile Engineering; Hálkova 6, Liberec 46117, Czech Republic, e-mail: jarmila.studnickova@tul.cz
[2] Ing. Lukáš Brázda, Institute of Chemical Technology Prague, Department of Glass and Ceramics, Faculty of Chemical Technology, Technická 5, Prague 16628, Czech Republic, e-mail: lukas.brazda@vscht.cz
[3] Prof. Ing. Aleš Helebrant, CSc., Institute of Chemical Technology Prague, Department of Glass and Ceramics, Faculty of Chemical Technology, Technická 5, Prague 16628, Czech Republic, e-mail: ales.helebrant@vscht.cz
[4] Doc. Ing. Petr Exnar, CSc., Technical University of Liberec, Department of Chemistry, Faculty of Education, Hálkova 6, Liberec 46117, Czech Republic, e-mail: petr.exnar@tul.cz



1 – metal roller (positive electrode), 2 – reservoir of the polymeric solution,
3 – polymeric solution, 4 – direction of fiber formation, 5 – textile substrate (support material),
6 – electrode grounding shield

Figure 1: *The patented principle of nanofiber production from polymeric solution [2]*

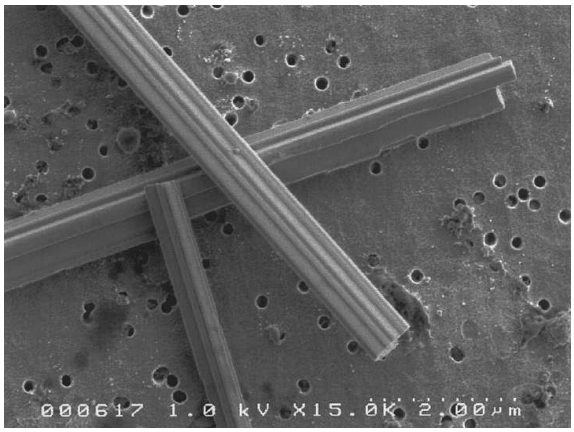


Figure 2*: Asbestos (Amosite) after 90 days in the rat lung [3]*

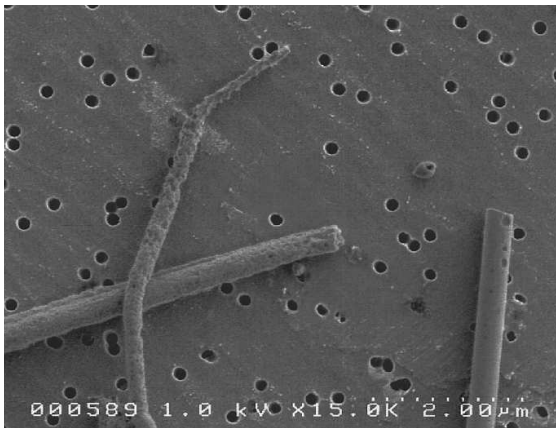


Figure 3: *HT Stonewool (MMWF34) fibers after 7 days in the rat lung [3]*

2. Experiments

The first inorganic nanofibers produced in the pilot plant were pure silicon oxide nanofibers. The principle of their production is the spinning of a polymeric solution prepared by the sol-gel method. The polymeric solution was electrospun on a device in the pilot plant in the Department of Nonwovens, Technical University of Liberec. [4] The nanofiber web was electrospun on nonwoven poly(propylene) support material, removed (Figure 4), and then heat treated at 180 °C. The results shown in Table 1 and Figure 5 demonstrate that the nanofibers' diameter is well reproduced during repeated preparation of nanofibers. The statistical tests confirmed that both prepared materials' best fit is lognormal distribution.

The first nanofiber sample produced, labeled J11-II, was used for preliminary tests of dissolution in simulated pulmonary fluid. The results have already been published. [5] The second nanofiber sample produced, labeled J18, was used to determine the specific surface

area by a nitrogen adsorption method. The specific surface area was 10.6 $m^2.g^{-1}$ and the pore volume of the pores with a diameter of less than 25 nm was negligible. These results correspond with the theoretical calculation of specific surface area. The theoretically calculated specific surface area of non-porous nanofibers with a diameter of 160 nm is 11.4 $m^2.g^{-1}$. Based on these findings, the J18 prepared nanofibers can be considered non-porous. Figure 6 shows Scanning Electrone Microscope snapshots of J18 nanofibers.

Figure 4: *Nanofiber web from J18 polymeric solution*

Table 1: *Statistical analysis of nanofiber diameters, considering lognormal distribution (QC Expert program)*

Sample	Mean diameter [nm]	Variance [nm^2]
J11-II	173	5613
J18	160	3811

In general, the inorganic nanofiber degradation is tested by “in vivo” or “in vitro” methods. The “in vivo” biopersistence tests measure the length of time it takes for half of the fibers placed into the test animal to be degraded ($t_{0.5}$). [3] The “in vitro” tests measure the speed of fiber dissolution in simulated pulmonary fluids.

Considering the size of the nanofibers, the “in vitro” methodology had to be modified and the results obtained by static and dynamic methods had to be compared. The method used was modified compared to the method used for preliminary results [5] of previously prepared J11-II nanofibers.

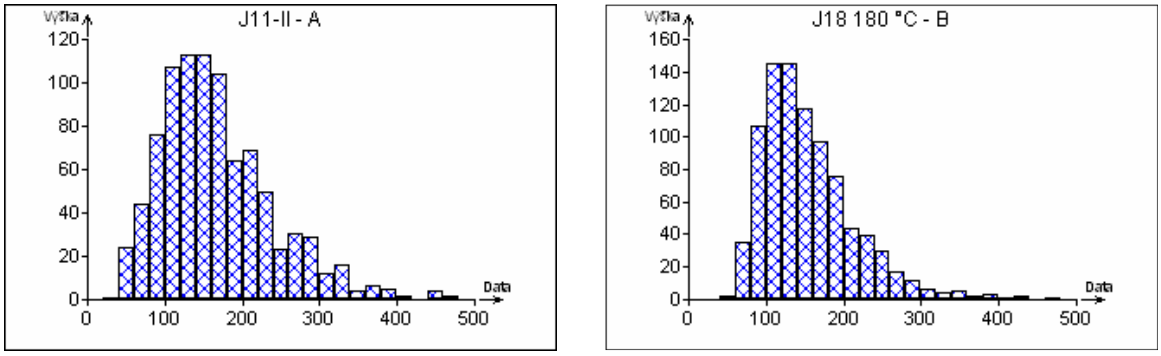


Figure 5: *Distribution of nanofiber diameters J11-II and J18 (x-axis displays diameter in nm, y-axis displays count)*

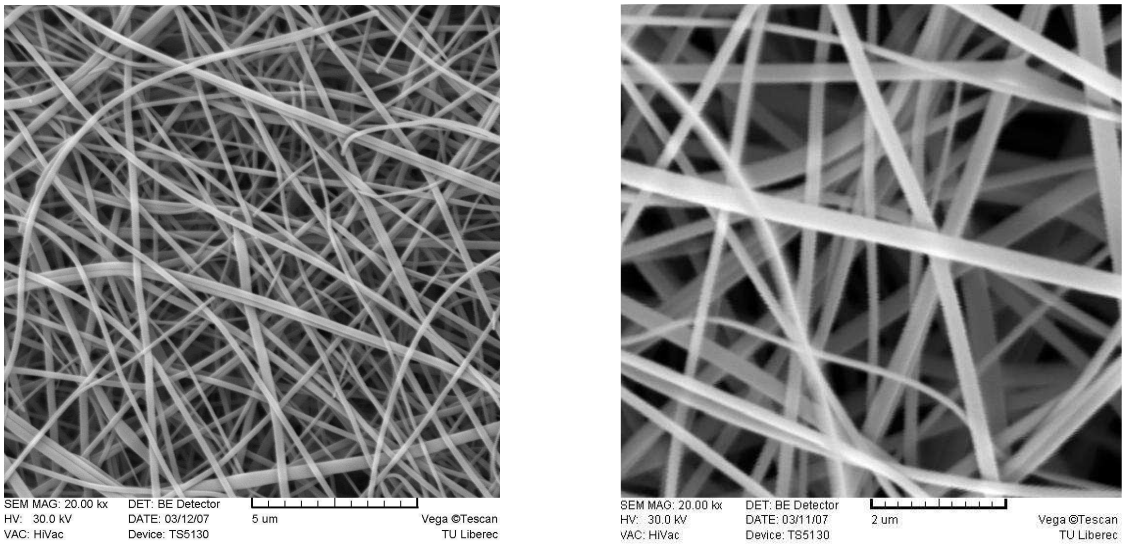


Figure 6: *SEM snapshots of J18 nanofibers*

To observe the solubility, the nanofibers were tested in distilled water buffered by TRIS (tris(hydroxymethyl)aminomethane) and HCl to a pH of 7.4. This corrosive solution can be used as an initial approximation of a simulated extracelular pulmonary fluid environment.

To measure the speed of dissolution, two test setups were used. During the static test, the weighted amount of nanofibers were inserted into a poly(ethylene) bottle and then corrosive solution was added. Because the corrosive solution did not flow nor was exchanged in this setup, its gradual saturation by corrosive products could happen, which in turn slows down the speed of dissolution. The dynamic test was used as the second setup. The continuous flow of fresh corrosive solution moved through the cell containing the tested material and simulated the flow of body fluids in the human body. This setup eliminates possible disadvantages of the static test. Both setups are schematically shown in Figure 7. The dynamic test was based on EURIMA methodology [6] for 48 hours at 37 °C. Two static tests were also done at 37 °C, lasting 48 hours and 7 days respectively.

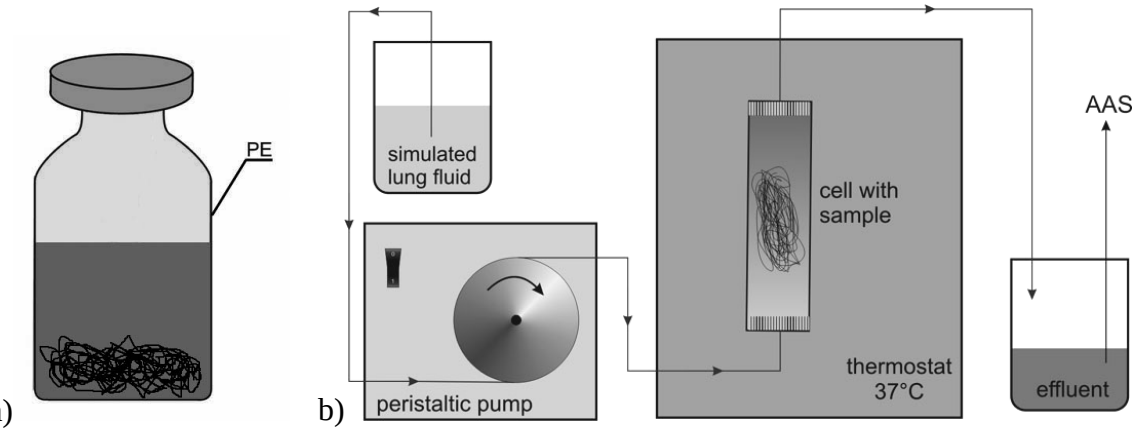


Figure 7: *a) static and b) dynamic setup of the corrosion test*

3. Results

The results of weight difference of the J18 nanofiber sample after its exposure to the corrosive solution are shown in Table 2.

Table 2: *Weight of fibers before and after exposure to corrosive solution (m_x is weight in actual time, dm is change of weight)*

sample		dynamic test			static test - 48 hours			static test - 7 days		
		1	2	3	A	B	C	D	E	F
m_0	[mg]	120.6	114.8	124.9	114.4	110.7	130.1	130.6	117.6	110.5
m_{48h}	[mg]	109.9	101.8	113.3	84.3	83.7	102.2			
m_{7d}	[mg]							70.4	57	53.5
dm	[mg]	-10.7	-13.0	-11.6	-30.1	-27.0	-27.9	-60.2	-60.6	-57.0
dm	[%]	-8.9	-11.3	-9.3	-26.3	-24.4	-21.4	-46.1	-51.5	-51.6

During the 48 hour dynamic test there was a 9.8 % weight loss which corresponds to 43 $ng.cm^{-2}.h^{-1}$. During the static tests the weight loss after 48 hours was 24.0 % (104 $ng.cm^{-2}.h^{-1}$) and after 7 days was 49.7 % (62 $ng.cm^{-2}.h^{-1}$). These results indicate that half of the weight of the nanofibers was dissolved in 7 days.

The study [7] implies that non-detrimental fibers are fibers with a dissolution speed in the order of tens to hundreds $ng.cm^{-2}.h^{-1}$. The so-called biosoluble fibers have dissolution speeds even close to 1000 $ng.cm^{-2}.h^{-1}$. The biopersistence of the tested nanofibers is close to HT Stonewool material [7] which is considered safe. Comparison of the dissolution speeds of different fibrous materials is in Table 3.

Table 3: *„In vivo“ and „In vitro“ tests comparison [7]*

Fiber	Type	$t_{0.5}$ [days]	R [ng.cm^{-2}.h^{-1}]
Crocidolite	Asbestos	**817**	**< 1**
Amosite	Asbestos	**418**	**< 1**
E Glass	FG Special App.	**79**	**9**
RCF1	Refractory Ceramic	**55**	**3**
475 Glass	FG Special App	**49**	**12**
Rock Wool	MW, MMVF12	**67**	**20**
JM 901	FG Bldg. Insulation	**14.5**	**300**
CertainTeed	FG Bldg. Insulation	**9**	**100**
Slag Wool	MW, MMVF11	**9**	**400**
HT Stonewool	MW	**6**	**59**

4. Conclusion

The speed of dissolution of silicon oxide nanofibers in simulated pulmonary fluid implies that during the static test half of the weight of the nanofibers was dissolved in 7 days and the speed of dissolution varied between 43 and 104 ng.cm^{-2}.h^{-1}. Due to these values we can see that the nanofibers are close to HT Stonewool material [7] which is considered safe. Considering that the nanofibrous material is quite new and so far determined speeds of dissolution are close to the minimum limit for safe materials, it is advisable to verify the reproducibility of these tests by conducting other “in vitro” tests, and eventually using “in vivo” tests to rule out its potential dangers.

Acknowledgments

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