

## THERMAL PROPERTIES OF SILICON OXIDE NANOFIBERS

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### Abstract

The purpose of this article is to collate and summarize our findings regarding the thermal properties of inorganic silicon oxide nanofibers. The nanofibers were produced by the electrospinning of a sol-gel prepared polymeric solution. The primary focus was on thermomechanical analysis (TMA), supplemented by IR spectroscopy and classical thermogravimetric analysis (TG). Two temperature ranges below 800 °C were identified when volatile constituents were liberated. The character of the constituents was determined by IR spectroscopy. The nanofiber morphology remained intact at 800 °C.

Key words: nanofiber, sol-gel, electrospinning, thermal properties

### Theoretical part

In addition to organic polymers, inorganic polymers can also be used for electrospinning, such as inorganic polymers prepared by sol-gel technology. By “sol-gel technology” we understand a group of methods of silicate and similar material preparation. The methods have the transformation of initial components (solution) to sol and then to gel by controlled hydrolysis and polycondensation in common. Homogeneity is preserved during this process [1].

The research objective was the preparation [2] and property characterization of inorganic nanofibers from pure silicon oxide by electrospinning. The polymer solution used was prepared by concentration of the initial solution, which was prepared by the sol-gel method under acid catalysis. The initial raw material for preparation of the polymeric solution was tetraethoxysilane and the solvent was isopropyl alcohol.

The nanofibers used in this study were produced by electrospinning on a Nanospider device in the pilot plant of the Department of Nonwovens [3,4]. The nanofiber web was deposited on the support material poly(propylene) and then separated again [2]. Electrospinning technology uses a strong electrostatic field to form nanofibers from polymeric solutions. Under these electrostatic forces, the droplet of solution is shaped to form a cone, known as the Taylor cone. Due to these forces a polymer jet is ejected from the tip of the cone and nanofiber is finally drawn. In contrast to previous methods, the Nanospider does not use any nozzles, spinnerettes or capillaries because these limit the production of industrial scale nanofibre webs. The Nanospider technology is based on the fact that it is possible to spin a fiber from a polymeric solution surface.

Figure 1 shows the schema of device which uses a rotating electrode submerged in a polymeric solution. Taylor cones are created on the electrode surface. Nanofibers are formed between the charged rotating electrode and an opposite grounded electrode.

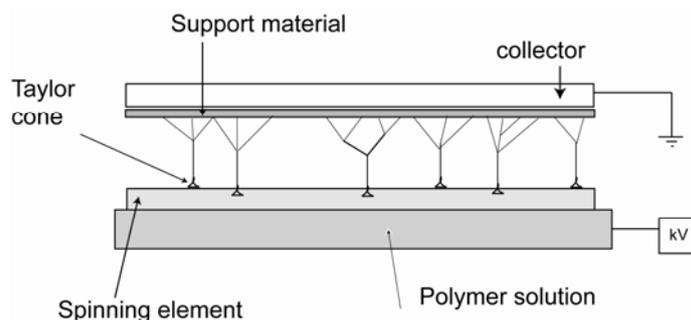


Fig. 1 : Generic schema of nanofiber web creation

### Experimental part

There was a dependency on temperature of thermomechanical properties observed on as-spun nanofibers [2]. The nanofibers had a mean diameter of about 180 nm. For thermomechanical analysis we used apparatus TMA CX04R (R.M.I.). The device registers differences in material dimensions (the nanofiber web thickness under constant thrust in our case) dependent on temperature under a constant speed of annealing. We used four different speeds of annealing (between 1 and 10 °C/min) for our measurements. Typical curves (Fig.2,3) show that there are two temperature ranges when dimension changes occur. The onsets and ends of these ranges depending on the speed of annealing are shown in table 1.

Tab. 1: Onsets and ends of ranges of web thickness change as determined by thermomechanical analysis (onset and end of ranges is defined by the point of intersection of the curve tangents as determined by device software)

	temperature for speed 1 °C/min [°C]	temperature for speed 10 °C/min [°C]
onset of first range (point 1)	72	117
end of first range (point 2)	136	197
onset of second range (point 3)	285	342

To further investigate the processes in these temperature ranges we used thermal analysis and IR spectroscopy. The results of thermogravimetric analysis (apparatus DMA DX047, R.M.I., operator Eva Černošková, University of Pardubice) imply that gas substance liberation during heating is happening also in the two temperature ranges (Fig. 4). These ranges are in accordance with ranges found by thermomechanical analysis. The measurement of thermal properties by DTA or DSC was not successful because we were not able to obtain reproducible results. These measurement issues can be explained by the very low thermal conductivity of the nanofiber web.

IR spectra measurements of the nanofiber web samples were done on FTIR spectrometer Spectrum-One with ATR accessory (Perkin-Elmer). We analyzed the spectra of three nanofiber web samples: as-spun nanofibers, heat treated nanofibers at 180 °C for 2 hours and heat treated nanofibers at 550 °C for 2 hours. There are bands related to organic compounds ( $2975\text{ cm}^{-1}$  and from  $1470$  to  $1380\text{ cm}^{-1}$ ), O-H bond vibration ( $1630\text{ cm}^{-1}$  and broad band at about  $3300\text{ cm}^{-1}$ ) and stretching vibration Si-O from Si-OH group ( $945\text{ cm}^{-1}$ ) which are clearly evident in the spectra. Other bands observed are related to stretching vibrations Si-O-Si. By comparing the three spectra (Fig. 5) we found that in the first temperature range when changes are occurring (observed by TGA at temperatures about 100 °C) only physically bound water is liberated. In the second temperature range of changes (about 350 °C) water bound as

Si-OH group is released as are the rest of organic compounds. After heat treatment at 550 °C there are no bands present in the IR spectrum other than bands related to amorphous SiO<sub>2</sub>.

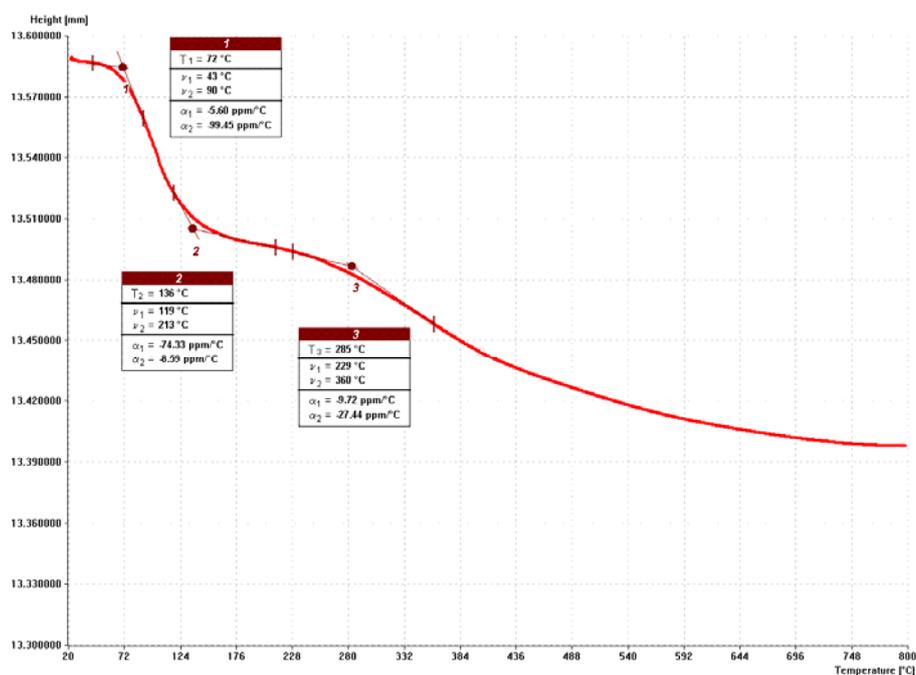


Fig. 2: Thermomechanical analysis of SiO<sub>2</sub> nanofibers (heating to 800 °C, speed of heating 1 °C/min)

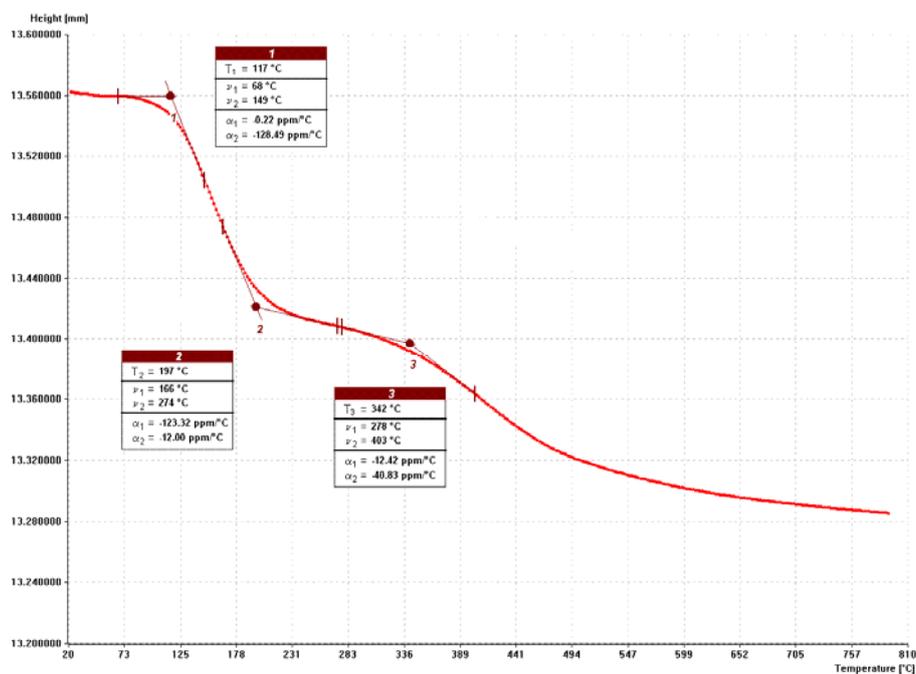


Fig. 3: Thermomechanical analysis of SiO<sub>2</sub> nanofibers (heating to 800 °C, speed of heating 10 °C/min)

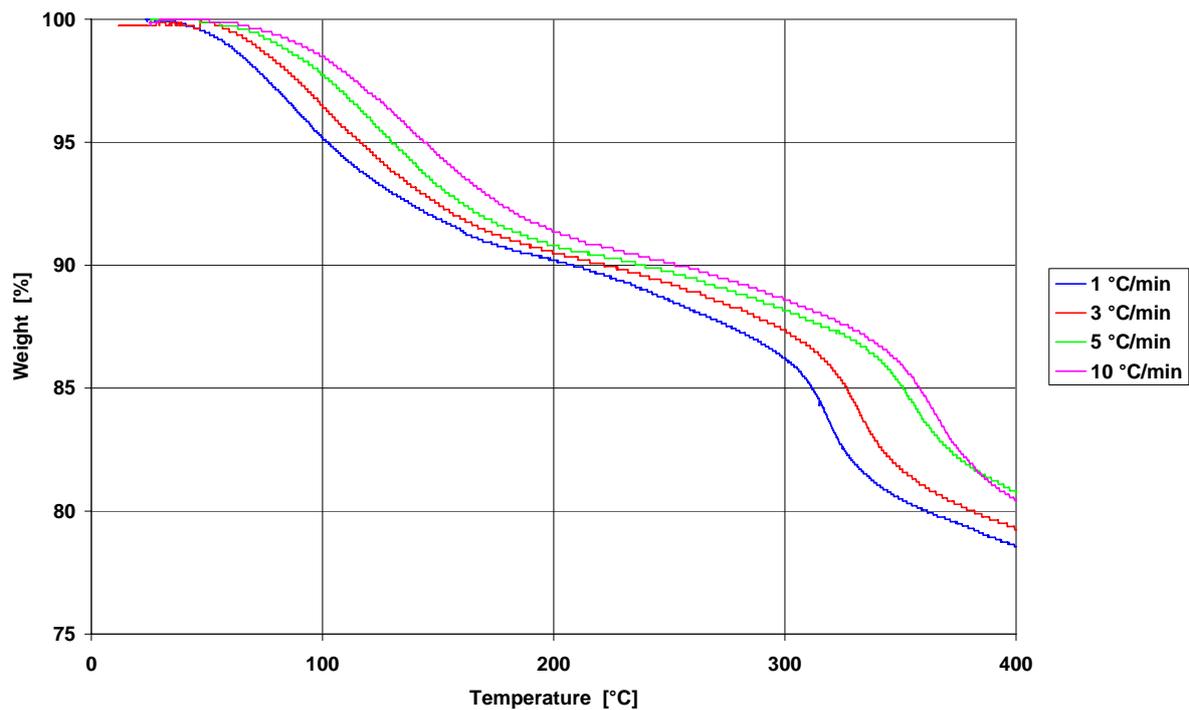


Fig. 4 : Nanofiber thermogravimetric curves depending on speed of annealing

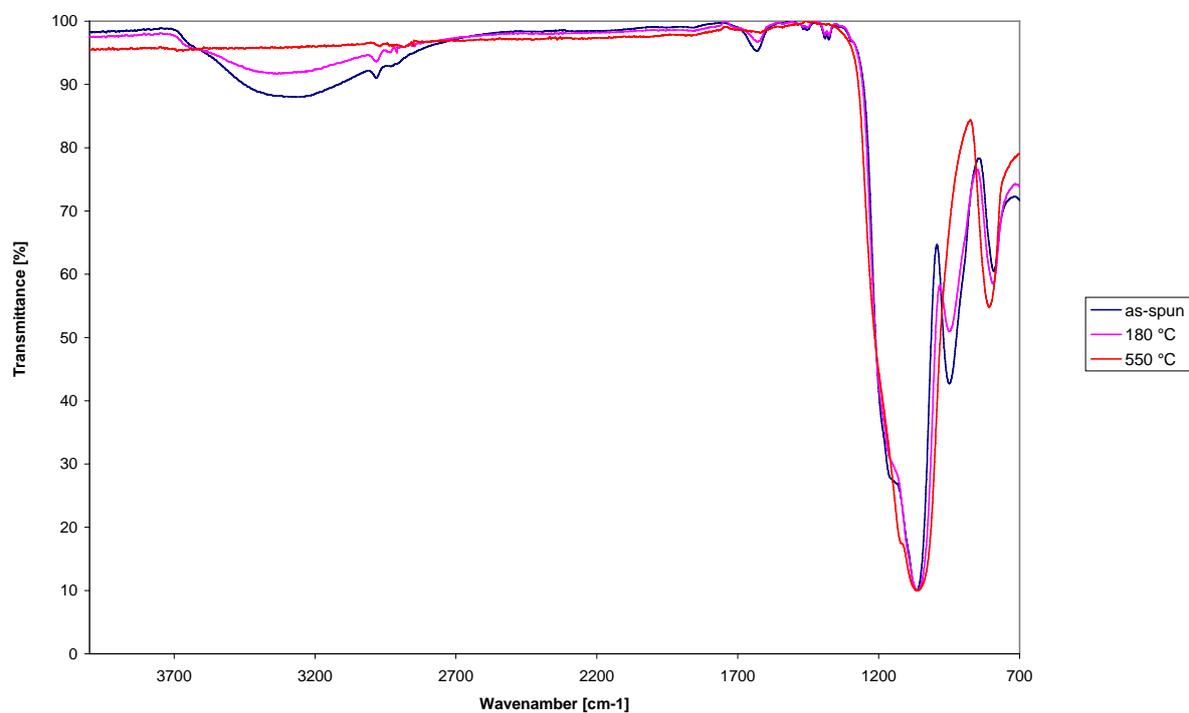


Fig. 5 : IR spectra of nanofibers after different heat treatments

The morphology of the initial nanofibers before tests is shown in Fig 6 and 7. The morphology is unchanged after heat treatment at 180 °C (Fig. 8). Fig 9 shows that there is some distortion of nanofibers after thermomechanical analysis up to 800 °C, but morphology remains intact.

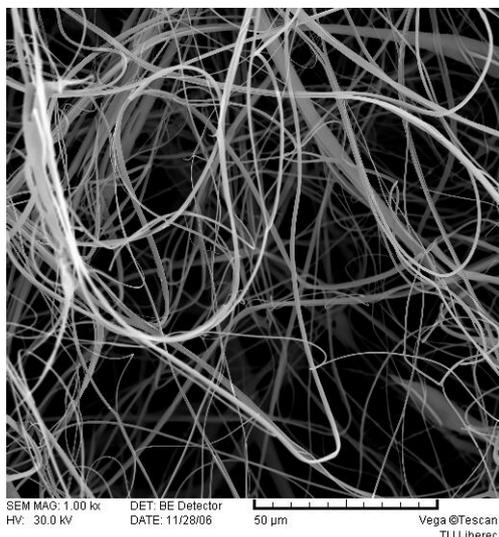


Fig. 6: SEM snapshot of SiO<sub>2</sub> nanofibers before thermomechanical analysis

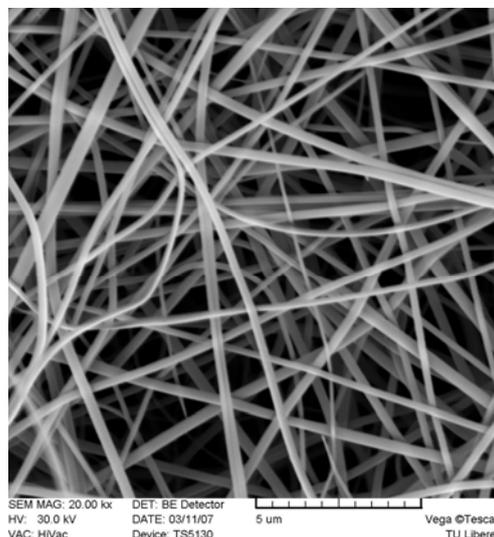


Fig. 7: SEM snapshot of SiO<sub>2</sub> nanofibers before thermomechanical analysis

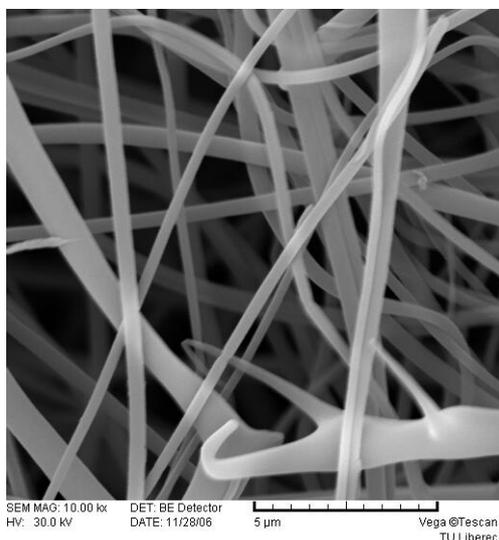


Fig. 8: SEM snapshot of SiO<sub>2</sub> nanofibers after thermal heating at 180 °C

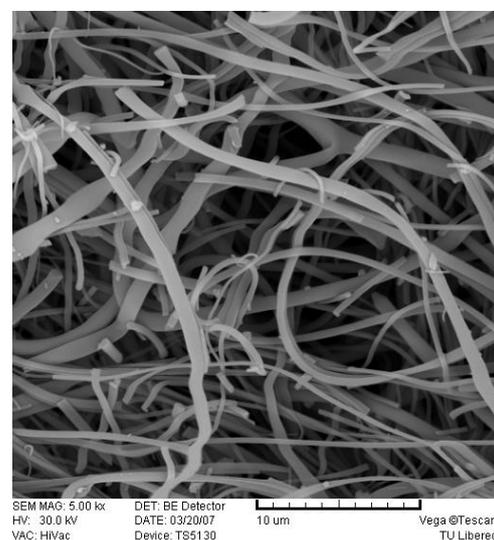


Fig. 9: SEM snapshot of SiO<sub>2</sub> nanofibers after thermomechanical analysis (800 °C)

## Conclusion

During heat treatment the SiO<sub>2</sub> nanofibers liberate water in two well-distinguished temperature ranges. Firstly, the physically bound water (at about 100 °C) is liberated,

followed by the water bound as Si-OH groups and the remainder of organic groups (at about 350 °C). The morphology of nanofibers however is not changed up to 800 °C.

### References

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