THE INCORPORATION OF INSOLUBLE ANORGANIC PARTICLES INTO POLYMERIC NANOFIBERS

Stanislav NEVYHOŠTĚNÝ, Jan GRÉGR, Eva KOŠŤÁKOVÁ

Technical university of Liberec, Studentská 2, Liberec

Abstract

Zirconium, cerium, praseodymium, hafnium, lead and bismuth tungstate particles were obtained via the reaction of heavy metal oxides and nitrates with tungstic acid. Particles were then ground and calcinated at 800 °C. After cooling, they were characterized by zeta-sizer and SEM-EDS. Particles were then ultrasonically dispersed in an ethanol solution of polyvinylbutyral and nanofibers were created from the mixture via the processes of needleless DC electrospinning and AC electrospinning. Obtained nanocomposite layers were tested for gamma radiation attenuation, using the ^{241}Am radionuclide as a source. Heavy metal particles were regularly distributed in the resulting materials and the attenuation of gamma radiation measured for the materials was significant.

Keywords: heavy metal, tungstate, composite, attenuation, gamma, PVB

1. INTRODUCTION

1.1 Origins

After a year 1895, when Wilhelm Konrad Roentgen discovered a radiation he called radiation X, many health problems appeared in reation to usage of the X ray. Incidentally, this was also the impulse to start the develepment of various X ray protective aparell and a whole new scientific branch – health physics. Despite numerous negative health effects, recognised even by great scientists like T.A. Edison, public didn't pay much attention to the protection and use of X ray grew every moment. It was in the year 1915, when British Roentgen Society finally came up with first precautions concerning the use of the X-ray. American Roentgen Ray Society adopted the rules seven years later. Since that time, the standard in the X-ray protection was lead-enhanced aparell.

1.2 Current situation

However, due to the scientific and technological advancement, it was possible to develop non-lead materials for the X ray protection. Thanks to the absence of lead, the materials are less toxic and the effect on the environment is much smaller. These materials are also lightweight, which has a positive effect on the user, which is an important advantage, especially during long procedures. Downside of these materials is their cost, significantly higher than traditional lead. The first nonleaded material was introduced in the year 1992 and was called Xenolite-NL. Despite the number of new technologies and materials, Xenolite is still a high standard today.

1.3 Aim

The aim of this work is to develop a new, lightweight composite nanomaterial, capable of attenuating X-ray of energy up to 150 keV, while not being harmful to the environment or personel. The material should be composed of polymeric nanofibers and heavy metal nano/micro particles. The material's structure is to be characterised by available methods, mainly SEM, and it's X-ray attenuation capability is to be measured.

2. INCORPORATION INTO POLYMERIC NANOFIBERS

2.1 Method

Due to several factors, the material chosen for the nanofibers was polyvinylbutyral (PVB). The diameter of PVB nanofibers is usually in several hundreds of nanometers, which corresponded very well with particle size. Using DC and AC electrospinng, 10 % ethanol solutions of PVB, containing 5 % of heavy metals particles, were processed into nanofibers. It was therefore also possible to test and compare the potential of AC electrospinning for the production of the material. Because hafnium and zirconium were not the primary subjects of research and exhibited some unwanted behavior such as strong sedimentation and agglomeration, they were not included in the experiment.

1.86 g of heavy metal particles were dispersed in 40 ml of pure ethanol using ultrasonic mixing. Then 3.72 g of PVB (Mowital® B 60 T, Kuraray America, Inc.) was added and again ultrasonically mixed.

Despite high viscosity of the polymer solution, a quite strong sedimentation of the particles was observed. For the DC electrospinning was therefore used a special-shaped electrode with thorns, which allowed continuous mixing of the solution, that by small amount reduced the sedimentation. The voltage used for DC electrospinning was 50 kV and the distance between the electrode and collector was 140 mm. The relative air humidity during the electrospinning was 30 % and the room temperature was 25 °C. The resulting composite nanomaterial layers were homogenous and exhibited no signs of coloration and therefore no solubility of the heavy metal salts in ethanol.

For AC electrospinning, the used voltage was 30 kV with frequency of 50 Hz. It was, however, not possible to prepare a homogenous structure, be it a layer or a thread. While PVB is a good polymer for processing by AC electrospinning, with addition of heavy metal particles however, the stream of nanofibers collapsed and was not continuous. This process, if optimized, could provide the means to prepare a nano-thread, suitable even for weaving.

2.2 Products

The first processed sample was the PVB solution with addition of dispersed particles of cerium tungstate. SEM showed, that inside the polymer fibers with diameter between 500 nm and 1000 nm, up to ten times larger particles were immobilized. This also shows, that despite ultrasonic dispersion of particles in the solution, the aggregation of small particles was still quite high. While viewing the sample in chemical contrast, it is visible, that the distribution is even is the whole nanofiber layer. The EDS analysis has shown the amount of heavy metals in the composite material to be about 5 % of the mass. The real amount of the heavy metals is however significantly higher (estimated at about 20 %) and the error is caused by the use of carbon tape to fix the sample in the microscope.

The second sample, PVB nanofibers with praseodymium tungstate particles, yielded uniform fibers with diameter about 1000 nm. The distribution of the particles throughout the whole sample is, same as in case of the first sample, even. The SEM has shown, that the whole surface of the particles immobilized in the fibers is coated with a layer of polymer. This should eliminate the possibility of particles being released from the structure and the exposure of the user to the heavy metals would therefore be negligible. EDS analysis have shown the amount of heavy metals to be 10 % of the mass (same as in case of the first sample, this result is also inaccurate due to the usage of carbon tape, but it clearly shows the amount of heavy metals is greater in second sample).

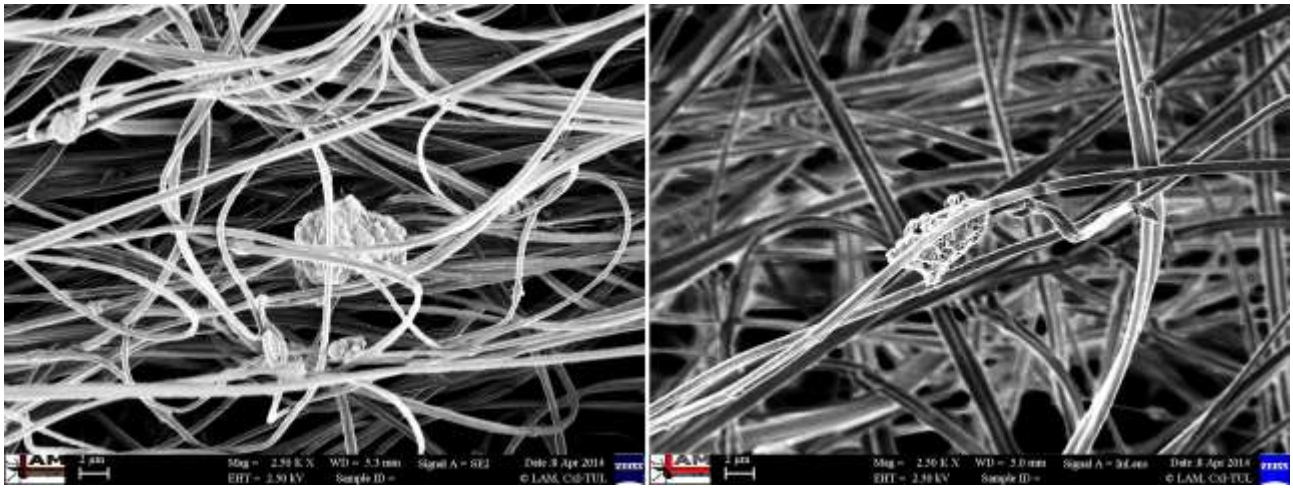

Fig. 1 Cerium (left) and praseodymium (right) tungstatates within PVB nanofibers, topographical contrast

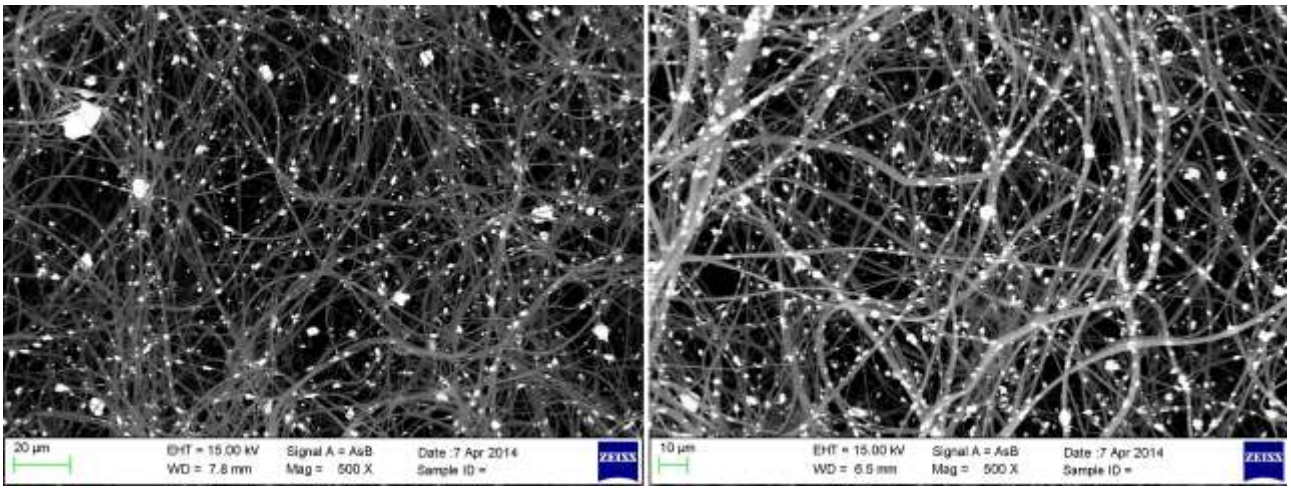

Fig. 2 Cerium (left) and praseodymium (right) tungstatates within PVB nanofibers, chemical contrast

Third sample, PVB solution with lead tungstate particles, yielded polymer fibers with diameter from 700 nm to 1000 nm. Many fibers also formed “bundles“. SEM has again shown the encpsulation of particles much larger than fiber diameter (Fig. 3, left), which incidentally again shows high agregation of particles. Despite the number of large agregates, there was also significant amount of dispersed particles with dimensions smaller than fiber diameter. The BsE view shows many of these particles don't even disturb the mophology of the fiber's surface. The EDS analysis have shown the amount of heavy metals to be same as in case of cerium tungstate particles.

Morphology of the nanofibrous layer with bismuth tungstate particles was very similar to that of previous sample. The fiber diameter was about 700 nm and fibers often formed “bundles“. It was again clearly visible, that besides larger particle aggregates, there was a significant amount of small particles scattered through the structure. The EDS analysis, however, has shown, that the amount of heavy metals in the material to be lower than in previous samples (only about 3.5 %).

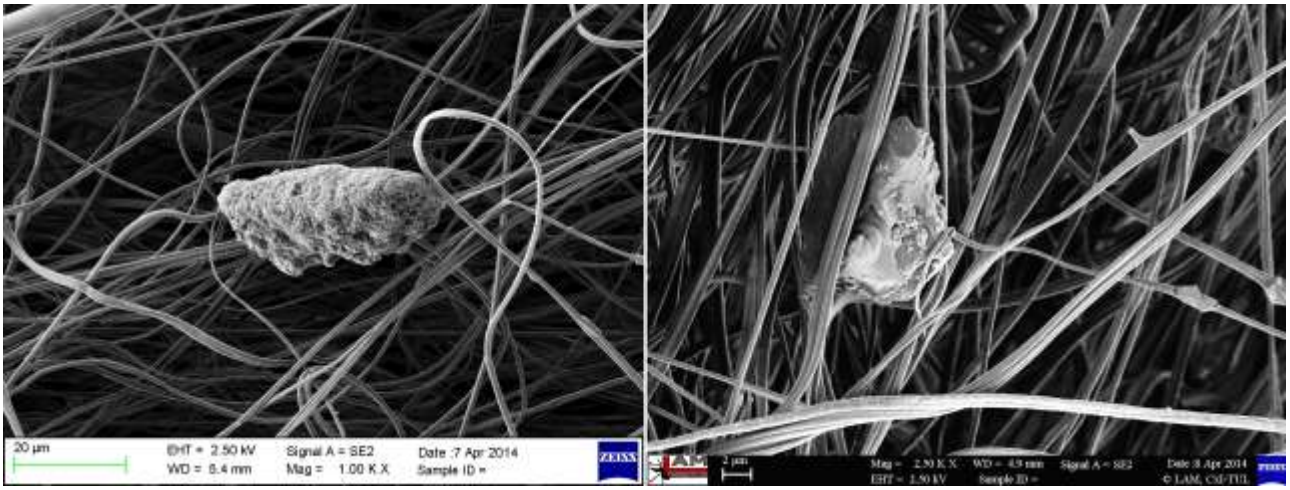

Fig. 3 Lead (left) and bismuth (right) tungstatates within PVB nanofibers, topographical contrast

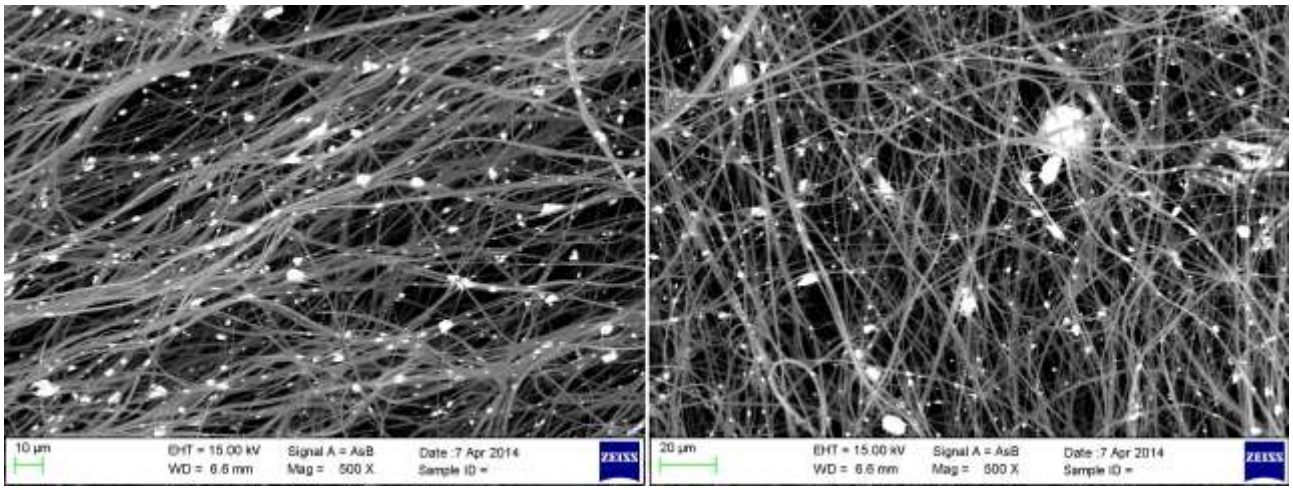

Fig. 4 Lead (left) and bismuth (right) tungstatates within PVB nanofibers, chemical contrast

3. GAMMA RADIATION ATTENUATION

3.1 Instrumentation

Due to better accessibility, gamma radiation was used instead of X-ray. The attenuation measurement was done using the ČEZ Gamabeta (1995) set with discrete source of radiation - ^{241}Am and Geiger – Müller detector. The initial tests showed, that prepared nanocomposite layers undeniably have certain potential for gamma/X-ray attenuation. The greatest attenuation ability was observed at the nanofibrous layer with integrated particles of praseodymium tungstate.

3.2 Method

The first step was to measure the background radiation values and the ^{241}Am radiation values without any shielding. Then, attenuation measurements were made with 1, 2, 4, 6 and 12 layers of obtained material placed between the radiation source and the detector. Every layer contained 0.16 g of heavy metal compounds per square meter. Each measurement was repeated twenty times and each lasted a hundred seconds.

The lowest attenuation was observed with the particles of lead tungstate. The plot shows an increase in the amount of detected radiation when 1, 2 and 4 layers of material were used. This shows the radiation was

probably dispersed, but the lower energy hits were still registered by the detector. When using 12 layers though, the attenuation was already almost 10 %. Similar results were achieved also with the layers imbued with bismuth tungstate. The attenuation of up to 25 % was measured when using the nanofibrous layers imbued with cerium and praseodymium tungstate. In the end, 40 layers (10 layers of each sample) were used as a shielding. The measured attenuation in this case was 46 %.

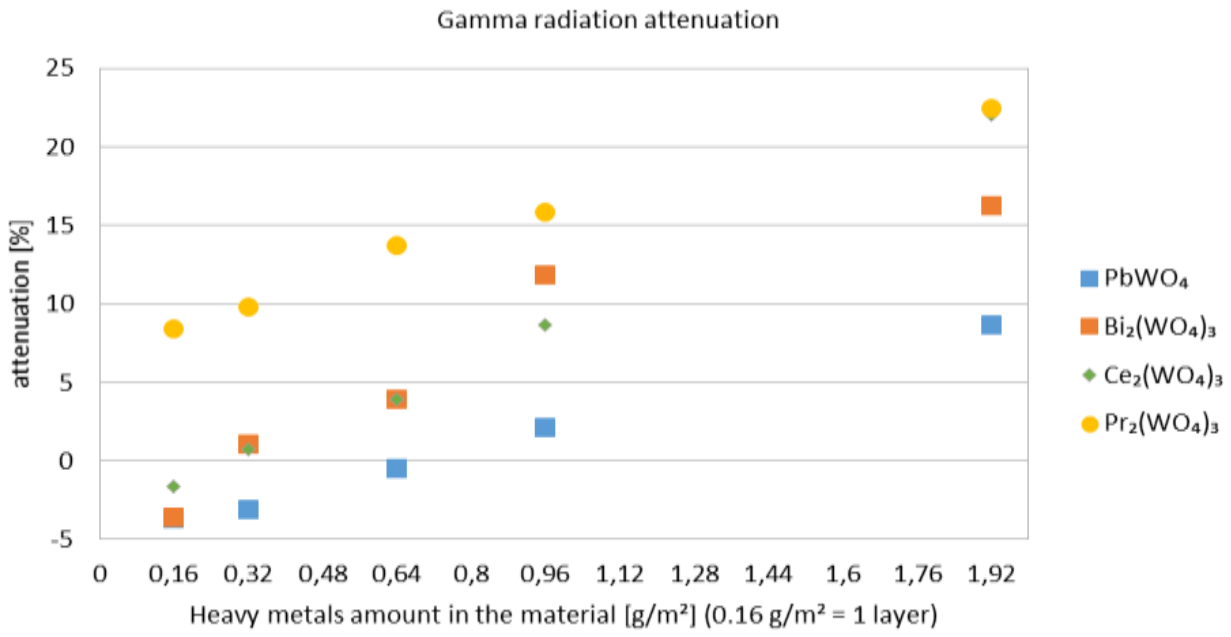

Fig. 5 Gamma radiation attenuation while passing through the layers of composite material

Because praseodymium tungstate exhibited the highest attenuation, it was also measured spectroscopically with range of 0 to 30 keV. The radiation source was same as during the measurement with Gamabeta set. This measurement confirmed the effectiveness of this layer for radiation attenuation.

4. CONCLUSIONS

Tungstic acid salts of several heavy metals were prepared in the progress, which were then integrated into nanofibrous structures of polyvinylbutyral. The heavy metals were selected according to several criteria: density, atomic number, mass attenuation coefficient, solubility and toxicity.

The morphology of the prepared powdered materials and resulting composite nanomaterials was investigated using scanning electron microsopy with EDS analysis. The particle size before integration into nanofibers was also investigated using zetasizer. The results show, that it is not necessary to process cerium, bismuth, zirconium and hafnium tungstate particles by mechanical grinding, because their dimensions were already below the required 1000 nm. Mechanical grinding was only required with praseodymium and lead tungstates. During electrospinning, the biggest complication was a strong sedimentation and aggregation of smaller particles. Despite the strong affinity to aggregation, the particles were evenly distibuted and well immobilised in the fibrous structure.

All created materials exhibited good potential for gamma radiation attenuation. Measured values did not correspond with the theory of Beer-Lambert's law, which was probably caused by radiation being scattered on the nano-sized particles.

The obtained data definatelly show an application potential for the material. Further research of the materials and methods for their preparation should concentrate on lowering the aggregation and sedimentation of

particles in the dispersion as well as increasing the amount of heavy metals in the composite material. Optimalization of AC electrospinning process could also yield a possibility of producing functionalized wowen nanofiber fabrics.

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