RARE EARTH ELEMENTS OXIDES NANOPARTICLES FOR IONIZING RADIATION ATTENUATION

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Abstract

Following up on a previous research, the aim of the work is to further investigate the possibility of using rare earth elements compounds in polymer matrix for ionizing radiation attenuation. Having proven the effectivity, the focus is primarily on the proper preparation and characterization of the materials and the effect on the stability of polymer solution and it's suitability for needleless electrospinning. The investigated materials in this case were the oxides of lanthanum, cerium, praseodymium, neodymium, gadolinium, holmium, erbium, thulium and lutetium. The methods of characterization used were solution conductivity measurement, x-ray fluorescence analysis, scanning electron microscopy, energy-dispersive x-ray spectroscopy and sedimentation time measurement in combination with Tyndall's effect.

Keywords: Attenuation, lanthanides, heavy metals, nanomaterial, electrospinning

1. INTRODUCTION

In our previous research, we have proven the ability of rare earth elements compounds (namely tungstates) to attenuate ionizing radiation. The measurement of gamma radiation attenuation by composite nanomaterial composed of polymeric fibrous matrix with incorporated nano and micro particles of inorganic compounds was done using a ČEZ Gamabeta set with radioactive americium 241 as a source of radiation. We came to a conclusion, that nanoparticles in the matrix in combination with larger agglomerates have a greater attenuation capability than bulk material, which does not correspond with Beer-Lambert's law. During our experiments, we utilized mostly extraordinary materials, not normally used for attenuation purposes.

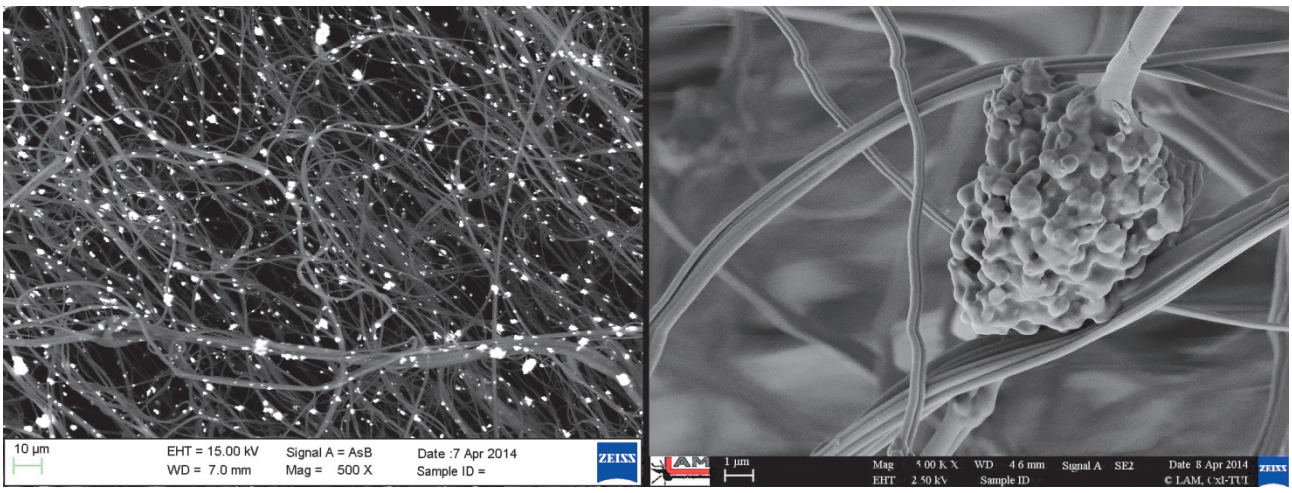

Fig. 1 Praseodymium tungstate particles in polymeric nanofibers, chemical (left) and topological (right) contrast

As to material preparation, the particles were first ultrasonically dispersed in the polymer solution while keeping their concentration at 10 wt%. At this concentration, the inorganic additives did not affect the DC electrospinning process stability. Successful experiments were also made with higher weight concentrations of up to 50 wt%. The powders were usually only treated by calcination, which was necessary for the production

of tungstates. Some were also additionally processed in a cryomill, which resulted in a decrease of mean particle diameter. In some cases however, a slight increase in particle size was observed. It has been accounted to stronger agglomeration tendencies of finely milled particles. Overall, the milling showed as generally beneficial, but not necessary.

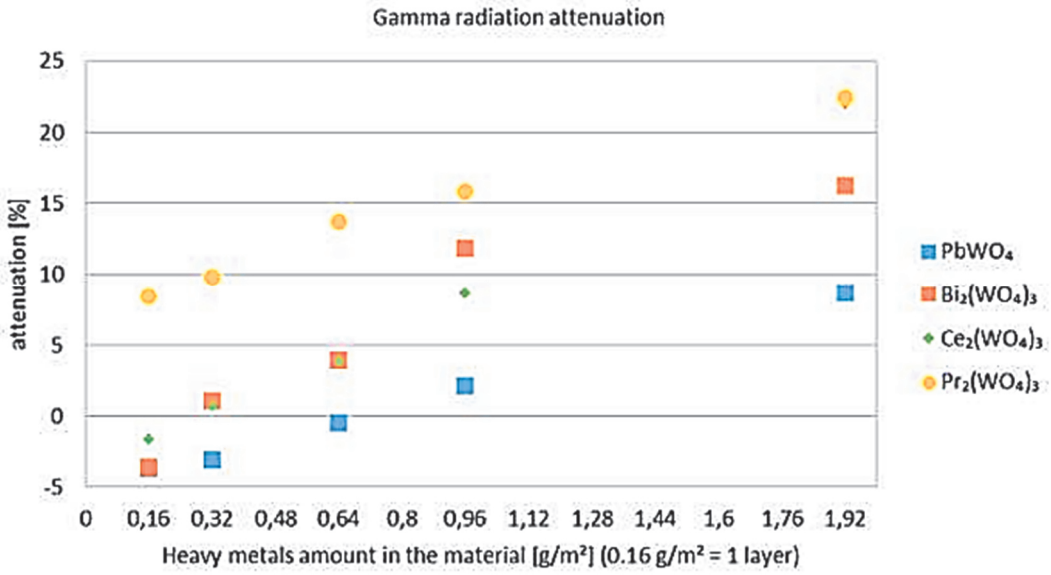

Fig. 2 Gamma radiation attenuation by a composite of polymer and heavy metal tungstates

The created materials had even distribution of particles in the material. A quite fast sedimentation and agglomeration were observed, due to the nature of the fine powders. Viewed under an electron microscope, it was visible, that apart from large agglomerates (several micrometers in diameter), much smaller particles were also scattered throughout the structure. Particles of all sizes were securely held in place by the polymer, which formed a layer on the whole surface of the individual particles. That means users will not come in contact with loose particles.

Due to the results obtained, we started focusing on rare earth elements oxides and tungstates. Those were chosen due to the attenuation ability being the function of atomic number, as well as density. Important factor is also the size of the individual particles in the polymer matrix. Our previous research has shown that because of the characteristics of nano and micro particles, the aggregation and therefore sedimentation (an undesired effect, but present also due to the high density) both occur at quite high rate, even in the viscous polymer solution. We found it however to be no obstacle for the production process - electrospinning from the dispersion of insoluble particles in polymer solution.

2. NEW MATERIALS

Because the research has proved the effectivity of combination of traditional attenuation materials like bismuth and lead with lanthanides, the further investigation is focused on the lanthanides themselves. Compared to other chemicals, lanthanides are scarcely used with only about 18 000 tons produced annually. About 85 % of the production is used in manufacturing catalysts and glass. Only a minor part of the production is used for more perspective areas, such as phosphors and magnets. Lanthanides are almost insoluble and practically unavailable in the biosphere. They are also not known to form any biological molecules. For these reasons, the elements and most of their compounds are classified as having low toxicity.

The materials were obtained from Crytur s.r.o. with further origin unknown. Crytur is a manufacturer of monocrystals for use as i.e. scintillation detectors, detectors for electron microscopy and laser rods. The quality of material was therefore supposed very high. The materials used were the oxides of rare earth elements

lanthanum, cerium, praseodymium, neodymium, gadolinium, holmium, erbium, thulium and lutetium. The mass attenuation coefficients of the compounds are visualized in the plot below. The peaks in the plots fill the area between 40 and 70 keV energy of gamma/x-ray radiation. While bismuth and lead would cover the attenuation on higher energies around 100 keV, it is desirable for the lower energies to be covered as well.

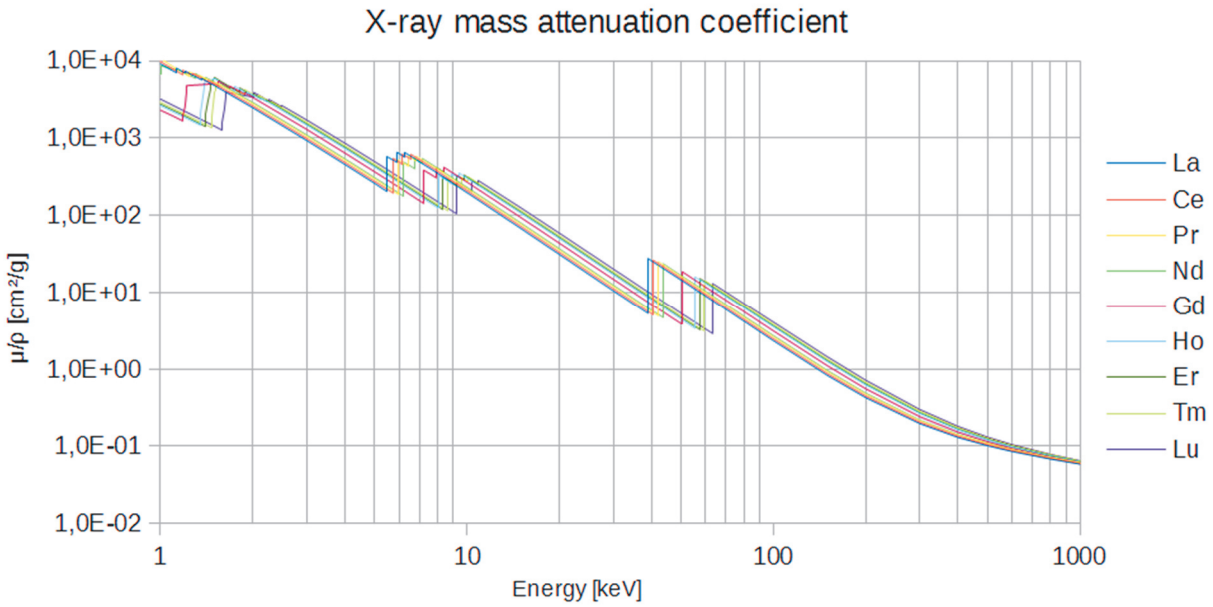

Fig. 3 X-Ray Mass attenuation coefficient (according to NIST; for elemental media)

2.1. Chemical composition

The composition of the materials was further investigated by means of energy dispersive x-ray analysis. The analysis confirmed the purity of the materials supplied by Crytur s.r.o. Analysis was performed using the Zeiss ULTRA Plus scanning electron microscope with Oxford Instruments EDS. The results show the heavy metal and oxygen ration to be as given without traces of other elements. It also indicates these are not hydrates of any sorts.

The materials were further investigated using x-ray fluorescence analysis (XRF). After the EDS analysis, the XRF analysis did not provide us with any new information. However, we could observe the spectra change when irradiating the sample with X-ray in atmospheric conditions, as opposed to EDS in a vacuum chamber. XRF analysis has usually shown a high content of other elements (usually other lanthanides with higher and smaller atomic numbers) in our samples, but having the results from EDS already, it was clear those are only interferences. However, they proved the capability of the powered chemical to disperse the X-ray radiation. The EDS analysis confirmed the oxides to be La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Gd_2O_3, Ho_2O_3, Er_2O_3 and Lu_2O_3.

3. PHYSICAL PROPERTIES CHARACTERISATION

Along with EDS analysis, the general observation and dimensions measurement were made using a scanning electron microscope. The measurement has, as expected, shown a significant number of larger agglomerates. However, it was possible to distinguish the small grains those were composed of. The smallest grains were usually only several nanometers and were observed in case of cerium, praseodymium, neodymium, gadolinium and erbium, for which the grain size was under 100 nm. The largest agglomerates for all the samples were about 10 μm.

While EDS provides good information about the particle dimensions and shapes, it only provides those for dry environment. For better understanding of how the powders will react in aqueous environment, a special apparatus has been constructed. This device consisted of 1 m long glass tube with an inner diameter of 8 mm.

On one end of the tube is a piece of a rubber hose, compressed with a pusher. Basically, this apparatus was a large capacity burette without the volume scale. Dispersions of particles were prepared by ultrasonically dispersing 2 g of the sample powders in 100 ml of distilled water for 1 minute. These dispersions were then transferred into the apparatus and were left to settle. The velocity of particles during the sedimentation was calculated using Stokes law for sedimentation.

$$v = \frac{(\rho_{sample} - \rho_{liquid}) \times g \times d^2}{18 \times \mu} \quad (1)$$

Using the formula (1), the time for particles of various sizes and densities to settle was calculated. Using the calculated values, we then tested the presence of submicron particles in the calculated distance from water surface in the tube. The tests were performed with a simple, yet informative Tyndall's effect - shining a laser beam through the dispersion. A LED laser with a wavelength of 405 nm was used to get the maximum amount of light diffraction in the dispersion. Using this simple method, we were able to confirm the presence of submicron particles in all the samples and a presence of nanoparticles (under 100 nm) in the majority of samples, namely in gadolinium, neodymium, praseodymium, erbium, cerium and lutetium oxides.

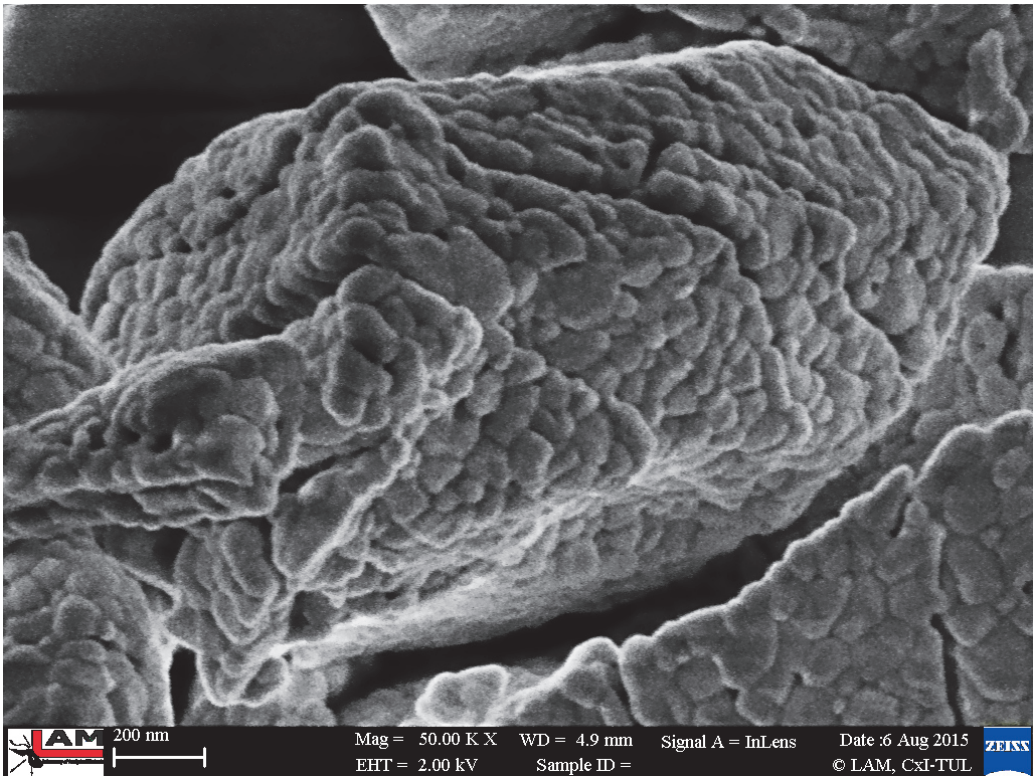

Fig. 4 Gadolinium oxide particle and grains

Another advantage of using this method was the homogenization of the dispersion. Using a thinner glass tube, about 15 ml of each sample was extracted from the top portion of the apparatus and transferred into a glass vial for further measurements, i.e. dimensions measurement using a Zeta-sizer. Also, by loosening the pusher at the end of the apparatus, it is possible to draw out the desired amount of dispersion containing mainly the coarser particles and separate those from the finer ones. By evaporation the water, several fractions of the original sample were obtained. The coarsest one is then processed by grinding to reduce the particle size before it is added back to the rest of the particles. The middle fraction is fit to be used as is. The finest particles are mainly suited for analytical purposes, due to a very low yield of the method.

Table 1 shows the specific sedimentation times and velocities for gadolinium oxide particles. Density of the oxide is 7.41 g/cm^3. For lower densities, the sedimentation times are longer, for higher densities they are shorter. Densities of all the samples were quite high, staring with lanthanum and praseodymium oxides with

6.5 g/cm^3, up to lutetium oxide with its density of 9.42 g/cm^3. A similar table was created for each individual oxide and Tyndall's effect was then investigated in the corresponding section of the sedimentation apparatus.

Table 1 Sedimentation times and velocities for Gd_2O_3 particles

d	v [m/s]	1 m		10 cm	
100 µm	3.6E-02	28.08	seconds	2.81	seconds
10 µm	3.6E-04	46.80	minutes	4.68	minutes
1 µm	3.6E-06	78.00	hours	7.80	hours
100 nm	3.6E-08	10.83	months	1.08	months
10 nm	3.6E-10	90.28	years	9.03	years

To be used for our purpose, it is also important to know the solubility of the oxides. Because solubility readily affects a conductivity of the solution, which affects the stability of the solution for electrospinning, the main factor in fact needed to be measured was the conductivity of a solution. The measurements were performed after sonically dispersing the particles, just before the dispersion was transferred into the sedimentation apparatus, using the Vernier LabQuest 2 with a conductivity probe set to the lowest measurement range. When measured, the conductivity for distilled water was found to be 5.1 ± 0.1 µS/cm. The values for individual dispersions ranged from 6.0 ± 0.1 µS/cm for cerium oxide to 11.2 ± 0.1 µS/cm for praseodymium oxide. The results indicate the solubility of the materials is extremely low to none and therefore would not affect the conditions of electrospinning. For comparison, the conductivity of similarly prepared sodium chloride solution would be over 12 000 µS/cm.

4. CONCLUSION

After investigating the properties of obtained materials, it was concluded these are suited to be used in further experiments. From previous experience, it was clear what properties should the material posses in order to provide the functionality and not disturb the manufacturing process. Almost all the samples were found to contain a small amount of nanoparticles, which provide increased functionality of the resulting composite material. Powders were found to contain an average amount of larger particles and agglomerates, which are necessary for the proper functionality of the material. Generally, the methods and criteria mentioned above should provide the necessary information to mark the material as suitable for use in this specific application. Ideally, the toxicity of the material should be as low as possible; otherwise the material may pose a threat to the user and/or the environment.

ACKNOWLEDGEMENTS

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