

POLYMER COMPOSITE NANOFIBERS

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Abstracts

Polymer composite nanofibers are formed from a polymer with inorganic nanoparticles. We deal with parameter combinations of nanoparticles, polymers, and solvents for the following electrospinning. Factors studied are the surface properties, size, crystallinity, density and toxicity of nanoparticles. Furthermore, we study changes in viscosity and in electrical resistance with increasing concentration of nanoparticles in solution. Polymeric composite nanofibers can be used, for example, for attenuation of the effects of ionizing radiation, magnetic sensors, biomarkers and so on.

Keywords: Composite nanofibers, inorganic nanoparticles

1. INTRODUCTION

Composite nanofibers are presented as polymeric nanofibers with inorganic particles. If we want the resulting product to have the best mechanical and other properties, we provide the means for synergy of surface of nanoparticles with a polymer. It is therefore a mutual option for a chemical bond, or at least the effective action of intermolecular forces. From the physicochemical point of view we need the surface energy of polymer, particles and solvents to be close values and not to differ too much to have even distribution of posts forming surface energy. For our own technology, we must observe a number of variables such as the size and the crystallinity of the nanoparticles. Furthermore, we have to study the changes in viscosity and electrical conductivity with increasing solids content of nanoparticles in the spinning solution.

Composite nanofibers of this type are addressed by many authors, in our work we are trying to achieve the highest concentrations of inorganic particles in the resulting fiber products. With generally similar issues dealt to a large extent Barakat [1], who formulated, that it is possible to prepare nanofibers electrospinning of colloidal solutions without much influence on the chemical composition of nanoparticles. In this work, however, greater amount of inorganics than the amount by weight of polymer solids is used. Li Wang [2] performed electrospinning successfully using PA66 with 5 - 7.5% montmorillonite. Kai Shen [3] generated bicomponent fibers with 2.5% hydroxyapatite nanoparticles. Marx [4] prepared PAN nanofibers containing Au for biosensors, which could also be covered by another layer of Au. Sheikh [5] prepared PUR nanofibers with 7-10% copper nanoparticles. Heikkila Pirjo [6] studied the incorporation TiO₂ nanofibers into PEO nanofibers. Many authors, eg.: Mincheva [7] dealt with the introduction of magnetic nanoparticles into PVA or other polymers. Ye [8] generated semiconductive nanofibers by incorporating the Pb²⁺ ions in polymeric nanofibers and their subsequent reaction with H₂S.

2. EXPERIMENTAL

Within our own experiments we used mainly polyvinyl butyral - PVB and polycaprolactone - PCL. As inorganic substances we tested acetylacetonates of Fe³⁺, Cr³⁺, Al³⁺, Co³⁺ Cu²⁺ and Co²⁺, tungstates of Sr, Ba, Zr, Ce, Pr, Hf, Pb and Bi and oxides - CeO₂, Fe₂O₃ and Fe₃O₄. The spinning experiment was performed by electrospinning from the needle, tip and a wire, followed also by AC electrospinning. Spinning conditions (voltage, distance, concentration) were set according to the optimum values for pure polymers. For testing and illustration of the products, FE SEM Carl Zeiss Jena Plus Ultra and the VEGA-3 TESCAN were used. Detecting the presence of particles in the fibers was determined by thermogravimetry TGA 500 TA Instruments. Control of viscosity of the solutions was performed using a rotational viscometer Haake Rotovisco 1 ThermoScientific. The electrical conductivity of the solutions was checked with InO Lab pH / Cond 720-Maneko probe.

3. RESULTS AND DISCUSSION

In all experiments, we succeeded in reproducibly preparing the nanofibers. As a proof of a perfect wetting of the solid nanoparticles in the spinning solution, the particles were completely trapped in the polymer structure - coated with a layer of polymer fibers. We tried to produce crystalline inorganic particles, smaller than the estimated diameter of the fibers (**Fig. 1, 2**).

At lower concentrations of acetylacetonates (1 part acetylacetonate to 2 parts of polymer), the resulting fibers are generally smooth and the hue of the corresponding basic color of acetylacetonate in solution (**Fig. 3**). Except the acetylacetonates of divalent metals (Cu^{2+} , Co^{2+}), which produced nanofibers with quickly formed crystals. Trapped crystals then formed inhomogeneities in fiber dimensions exceeding several times the diameter of nanofibres of polymer (**Fig. 4**).

The spinning solutions were homogenized using ultrasound probe just before spinning experiments. In some cases, however, particles have continued to agglomerate and relatively large bizarre inhomogeneities appeared in the resulting nanofibers (**Fig. 5, 6, 7, 8**). SEM images - Chemical Contrast - show regular distribution of the particles in the fibers (**Fig. 9**).

It is important to realize, that the inorganic particles usually had a high density. Therefore, at a relatively high weight content of the nanoparticles in the fibers, the volume filled by the particles is quite low. Densities of used oxides were about 5 g/cm^3 , the densities of used tungstates were over 7 g/cm^3 (**Fig. 10**). From the perspective of manufacturing of reinforced plastics in the macro scale, to complement the functional properties of the reinforcement, volume of the fillers should be higher than 30%. This, however, means more than 70% by weight of particulate content.

Another problem in the formation of polymer composite nanofibers is the sedimentation of particles in solution due to high density and therefore low stability of these solutions. Sedimentation rate according to Stokes equation is proportional to the density difference between the particle and the environment and the square of their radius. It is then inversely proportional to the viscosity of the environment. The viscosity of the spinning solutions should theoretically be increased with increasing volume fraction of the particles according to the Einstein relation. Because particles are not of spherical shape and the same size, the influence on viscosity is greater. We found that the spinning solution containing 10 wt% of Fe_3O_4 (2 vol%) had a viscosity of about 24% higher than the pure solution of the PVB. According to Einstein's equations, this increase should be about 5%. Shapes of Fe_3O_4 nanoparticles (**Fig. 1**) are octahedral with a certain size distribution. It is possible to achieve the slowest sedimentation of particles by smaller particle size.

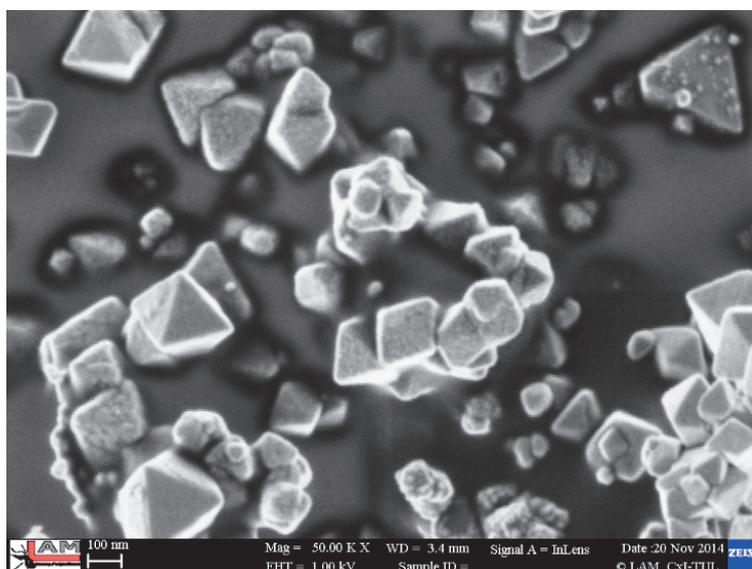


Fig. 1 SEM image of nanoparticles of Fe_3O_4

The inorganic nanoparticles can also influence the electrical conductivity of spinning solutions. Some of our other experiments with incorporating higher concentrations of metal nanoparticles into nanofibers were unsuccessful. Tested compounds are namely good conductors of electricity, with 10% by weight of Fe_3O_4 , the electrical conductivity of the solution more than doubled. Still we managed to prepare quality nanofibers without changing the electrical spinning conditions.

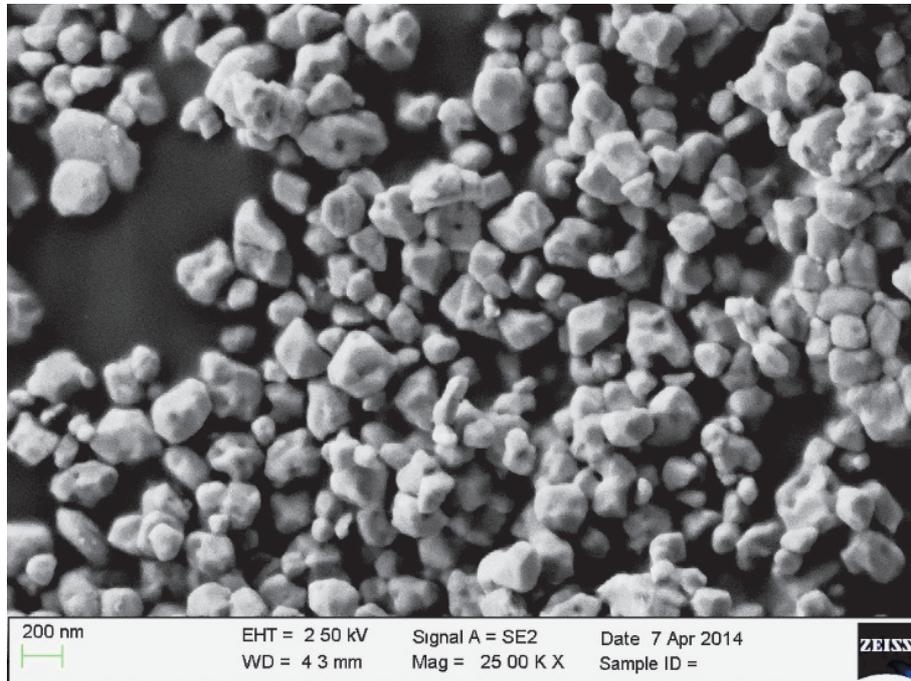
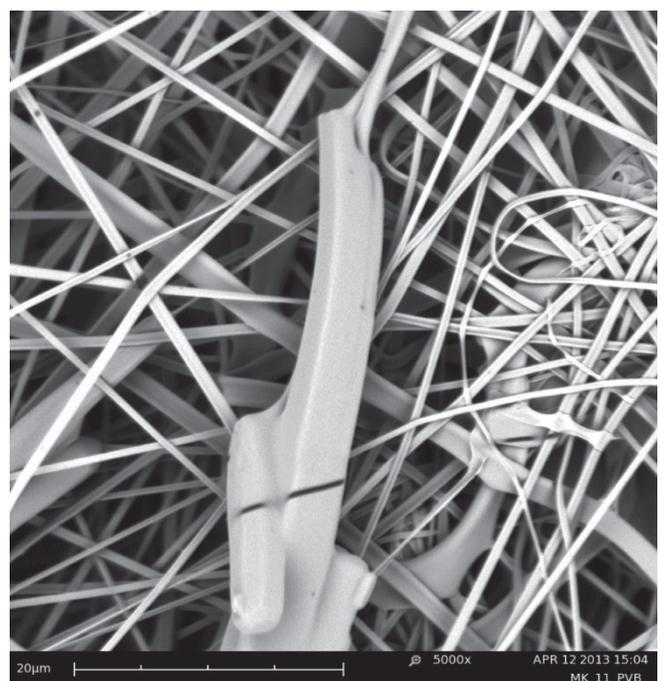
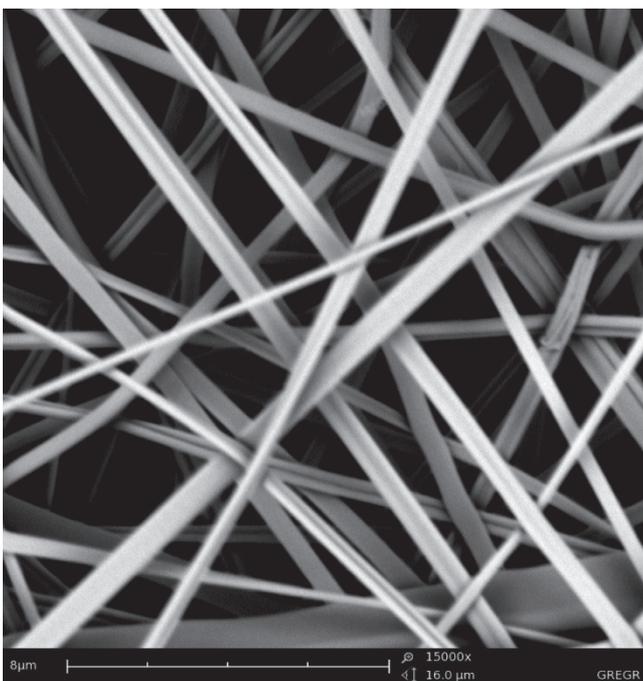
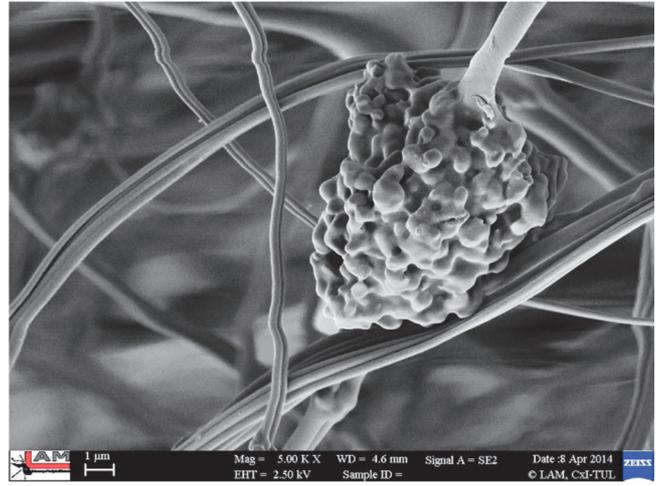
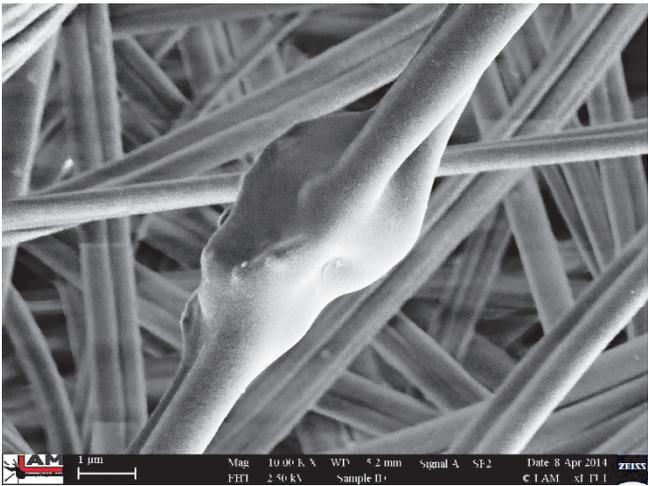


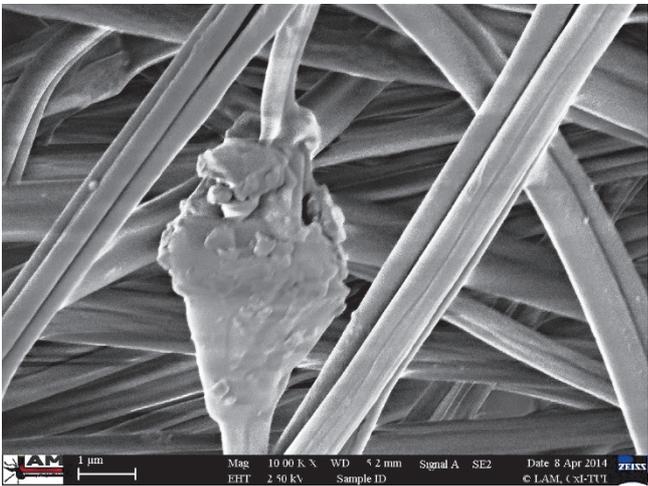
Fig. 2 SEM image of nanoparticles of zirconium tungstate



Figs. 3, 4 SEM image PVB nanofibers with Fe^{3+} and Cu^{2+} acetylacetonates



Figs. 5, 6 SEM image of PVB nanofibers with Bi³⁺ and Pr³⁺ tungstates



Figs. 7, 8 SEM image of PVB nanofibers with Bi³⁺ tungstates

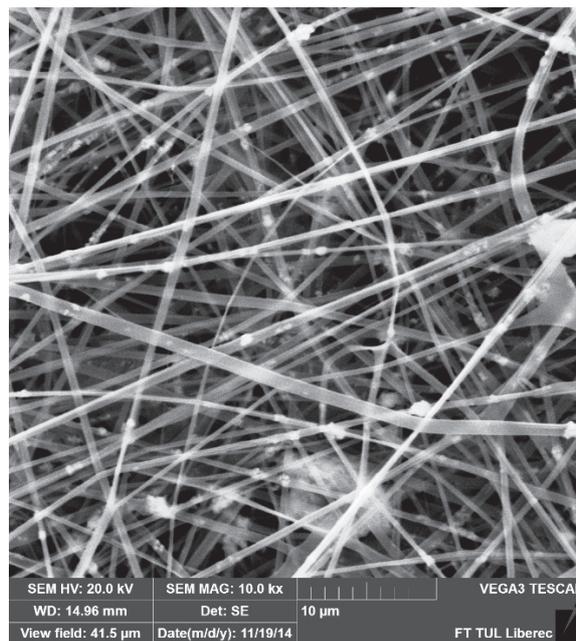


Fig. 9 SEM image of PVB nanofibers with Fe₃O₄ nanoparticles - chemical contrast

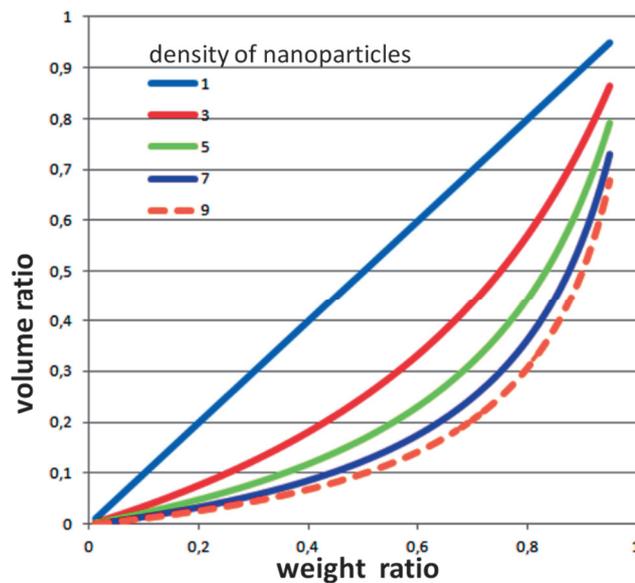


Fig. 10 Relation of weight and volume fraction of nanoparticles depending on their density

4. CONCLUSION

In our experiments, we verified that it is possible to prepare composite polymeric nanofibers with a higher content of inorganic nanoparticles. The condition for the creation of quality nanofibers is perfect wetting of solid nanoparticles by spinning solution. It is important to homogenize the spinning solution just before the electrospinning. Solid nanoparticles should have dimensions as small as possible to prevent sedimentation during the electrospinning process.

Resulting composite nanofibers will be used in biomedical fields, and in the formation of semiconductor and magnetic sensors and also as a material for attenuating the effects of ionizing radiation (X-ray and gamma-ray).

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