

POLYMER COMPOSITE NANOFIBERS

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Abstract

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

Keywords: composite nanofibers, inorganic nanoparticles

1. INTRODUCTION

Composite nanofibers want to present as polymeric nanofibers with inorganic particles. If we want to make the resulting product had the best mechanical and other utility features, we provide opportunities for synergies surfaces 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 to surface energy polymer particles and solvents were close values and did not differ too much even distribution of posts forming surface energy. For our own technology, we must follow a number of variables such as the size and the crystallinity of the nanoparticles. Furthermore, then 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. Quite generally, and to a large extent dealt with similar issues Barakat [1], who formulated, that it is possible to prepare nanofibers electrospinning of colloidal solutions without much influence the chemical composition of nanoparticles. In this work, however, used is always greater than the amount by weight of polymer solids. Li Wang [2] made electrospinning successfully PA66 with 5 - 7.5% montmorillonite. Kai Shen [3] generated bicomponent fibers with 2.5% hydroxyapatite nanoparticles. Marx [4] prepared for biosensors PAN nanofibers containing Au, which was possible covered 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 by the introduction of magnetic nanoparticles into PVA or other polymers. Ye [8] generated semiconductive nanofibers by incorporating of 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 Fe³⁺, Cr³⁺, Al³⁺, Co³⁺ Cu²⁺ and Co²⁺, and tungstate 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, hereafter by AC electrospinning. Spinning conditions (voltage, distance, concentration) were set according to the optimum values for pure polymers. To test and illustration of the products were used FE SEM Carl Zeiss Jena Plus Ultra and the VEGA-3 TESCAN. 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 probe Ino Lab pH / Cond 720-Maneko.

3. RESULTS AND ITS DISCUSION

In all experiments, we succeeded in reproducibly prepare nanofibers. If there was a perfect wetting of the solid nanoparticles in the spinning solution, the particles were completely trapped in the polymer structure, thus the particles were coated with a layer of polymer fibers. We tried to make inorganic particles were crystalline in nature and is smaller than the estimated diameter of the fibers (Fig. 1.2).

At lower concentrations acetylacetonates (1 part acetylacetonate to 2 parts of polymer), the resulting fibers generally smooth and the hue of the corresponding basic color acetylacetonate in solution (Fig. 3). Except the acetylacetonates of divalent metals (Cu^{2+} , Co^{2+}), which managed the creation of nanofibers quickly to form 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, have continued to particle agglomeration and the resulting nanofibers appeared relatively large bizarre inhomogeneities (Fig. 5, 6, 7, 8). SEM images - Chemical Contrast - show relatively regular distribution of the particles in the fibers (Fig. 9).

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

Another problem is in the formation of polymer composite nanofibers due to high density of the sedimentation of particles in solution, namely 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 too. 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 have not of spherical shape and the same size, the influence of viscosity is greater. We found that the spinning solution containing 10 wt% of Fe_3O_4 (vol2%) 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. The slowest sedimentation of particles, we can ensure that only the smallest possible particle size.

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

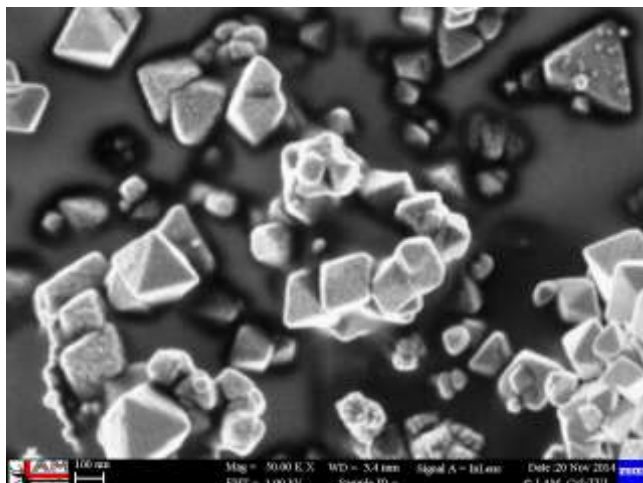


Fig. 1 SEM image of nanoparticles of Fe_3O_4 ,

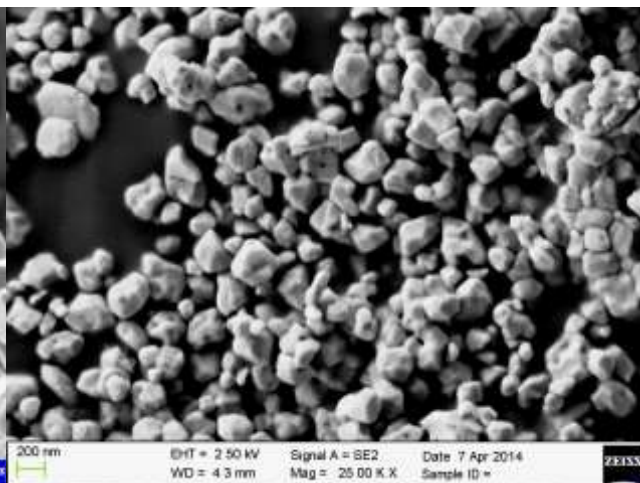


Fig. 2 SEM image of nanoparticles of zirconium tungstate

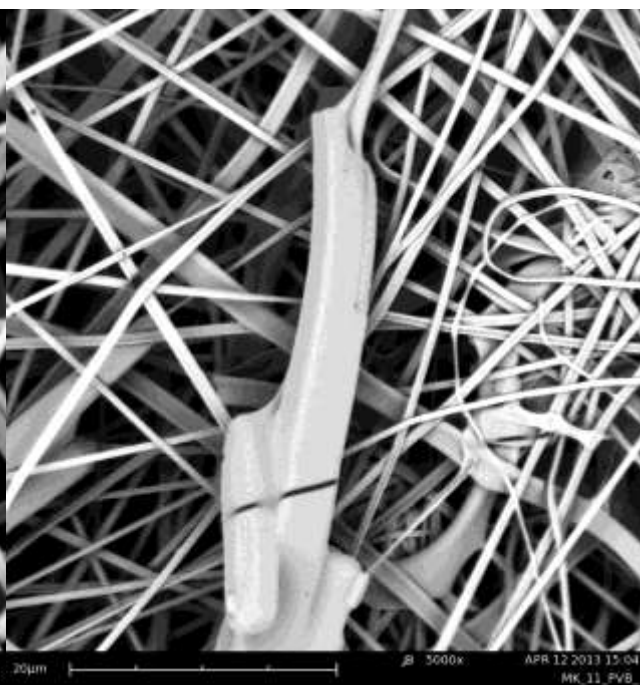
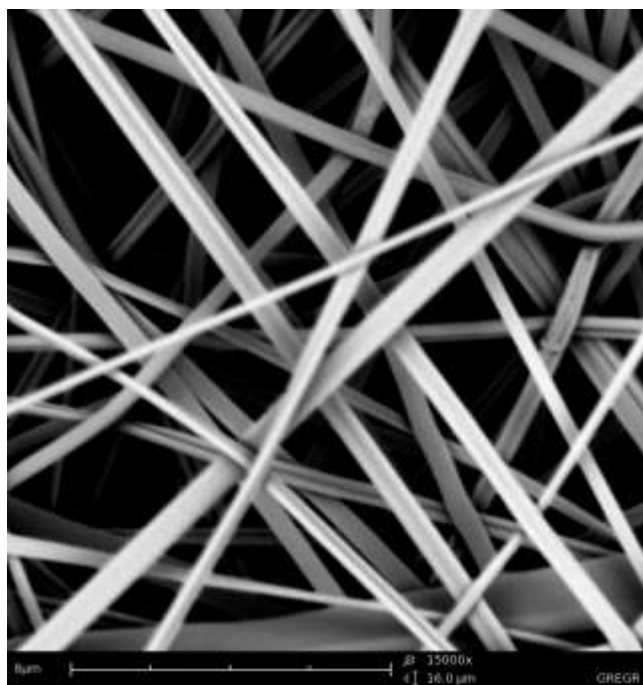


Fig. 3, 4 SEM image PVB nanofibers with Fe^{3+} and Cu^{2+} acetylacetonates

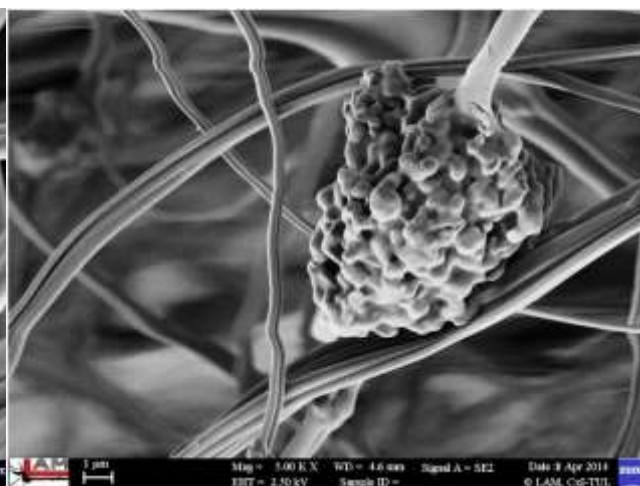
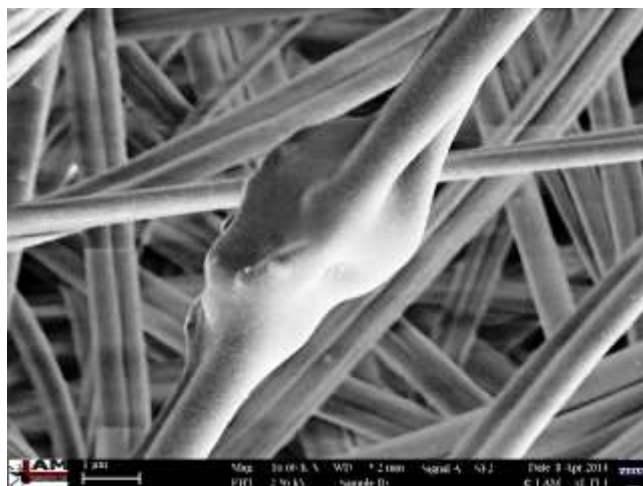


Fig. 5, 6 SEM image of PVB nanofibers with Bi^{3+} and Pr^{3+} tungstates

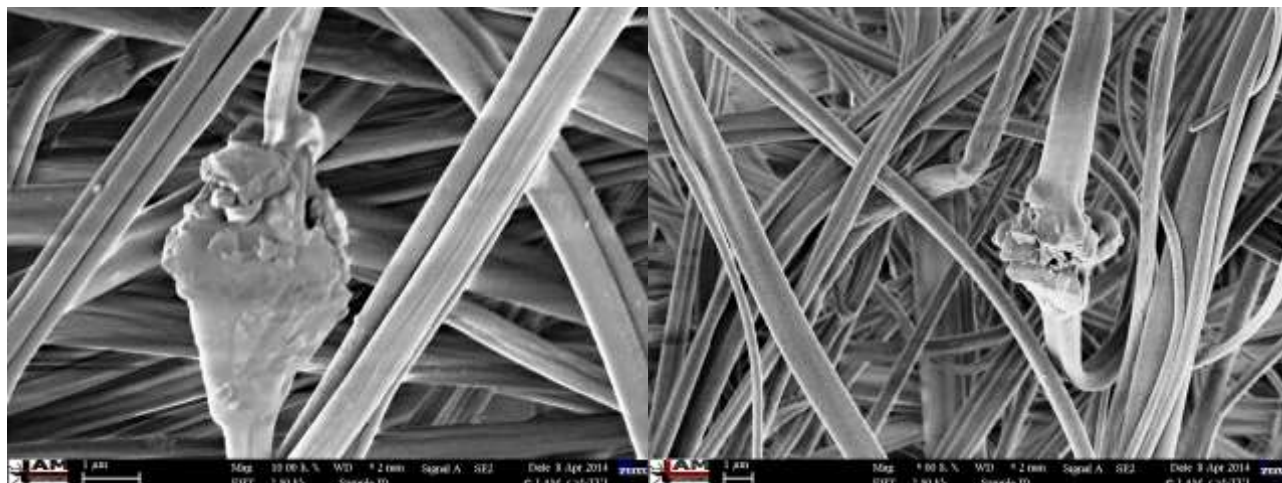


Fig. 7, 8 SEM image of PVB nanofibers with Bi³⁺ tungstates

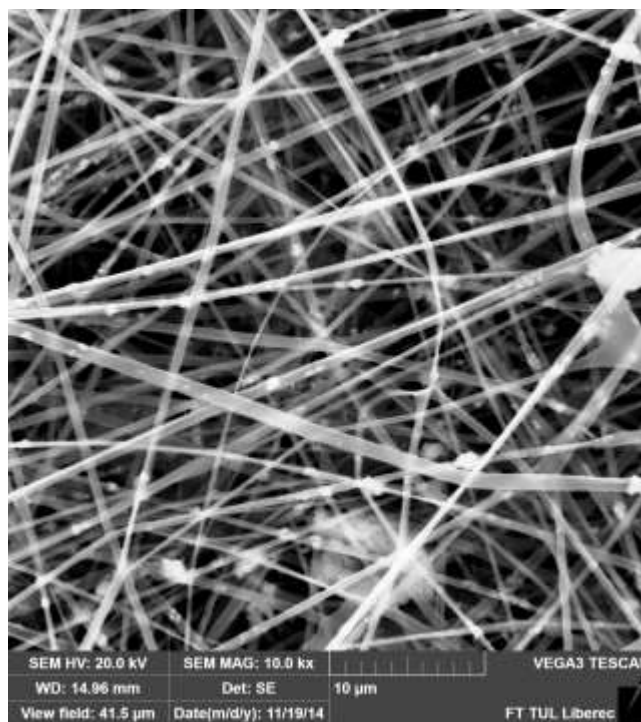


Fig. 9 SEM image of PVB nanofibers with Fe₃O₄ nanoparticles – chemical contrast

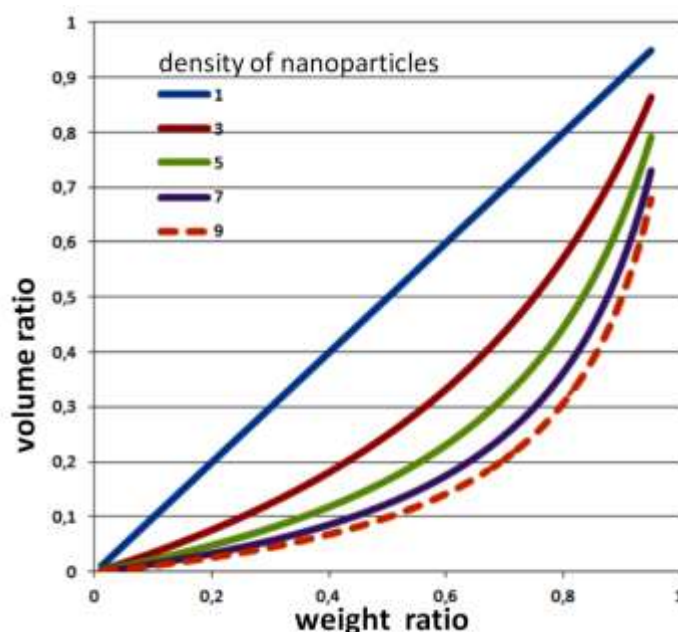


Fig. 10 Relation of weight and volume fraction of nanoparticles depending on their density

4. CONCLUSION

In our experiments, we verified that it is possible to prepare a polymer composite 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 homogenise the spinning solution just before the preparation of electrospinning fibers. Solid nanoparticles should have dimensions as small as possible to prevent to 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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