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Insertion of Cu Nanoparticles into a Polymeric Nanofibrous Structure via an Electrospinning Technique

Abstract

Nowadays, nanotechnologies are of great interest in many areas of research and textile materials are also the ones that are getting more and more involved into it. Recently researchers have started to concentrate on the insertion of different nanoparticles into polymeric structures and also on integrating fibrous nanostructures into more complicated systems. The aim of our research was to embed copper (Cu) nanoparticles into a nanofibrous structure via a sophisticated electrospinning technique. SEM and EDS techniques were used in order to evaluate the results of the experiments performed: the quality of the nanofibrous structure and the distribution of nanoparticles inside the fibres. Results showed that we succeeded in embedding Cu nanoparticles into polymeric nanofibres, despite the latter having formed when the polymer was moving upwards and the electric field between the electrodes in the electrospinning device was strong.

Key words: electrospinning, nanoweb, nanocomposites, nanoparticles, SEM, EDS.

Introduction

It is obvious that with the capability of tailoring materials at a nanoscale, it is possible to add multifunctionality to existing composite material systems. In the biological world, a cell is at a scale of a few to tens of micrometers in diameter. Viruses, ribosomes and antibodies are at a scale of tens and hundreds of nanometers. Nature has created many efficient nano systems. In previously studied areas nanotechnology was at the improvement stage, while at present some areas in terms of possibilities are just at the beginning. Current research activities include the nanocoating of surfaces for the guided migration, spread, growth and differentiation of cells in vivo and in vitro, as well as the development of nanofibre materials for wound dressing and drug delivery systems. All application areas of biomedical textiles continue to advance, but they all depend on the properties of the fibre and constructions fabricated from them [1 - 3].

Due to the small diameter, high surface area to volume ratio and high porosity, polymeric nanofibres can be used for the production of many devices, including medical prosthesis, scaffolds for tissue engineering, wound dressings, controlled drug delivery systems, cosmetic skin masks and in many other areas. Electrospinning is a versatile method that has been recently adapted for the engineering of different nano-fibrous structures for medical purposes. And yet, despite its introduction decades ago, the effect of process and material parameters on fibre

formation is still under theoretical and experimental investigation [4 - 13].

Nanocomposite is a class of materials that gains unique physical properties and a tangible application potential in diverse areas. Recently, intensive investigations of the incorporation of nanoparticles into polymeric fibres have been carried out. It is claimed that [14] by decreasing the size of particles, the effectiveness of additives increases, thus as a result the concentration of additives in the mixture can be reduced. Nanoparticles, as compared to microparticles, can be incorporated into fibres much more easily [14]. Interest in the dispersion of nanoscaled inorganic fillers in an organic polymer to form a polymer nanocomposite has significantly increased recently. An essential role in the application of nanocomposites, as in the case of any nanomaterial, is played by the ability to control the nanostructure. Novel properties of nanocomposites can be obtained by successfully imparting the characteristics of single constituents to the integral material. The most common procedure for the insertion of nanoparticles into polymeric fibres involves their incorporation into the polymer by physical means during fibre formation. The final constitution of the product (physical and chemical properties) differs from both pure polymers and inorganic fillers. So far most of the studies carried out have concentrated on a combination of polymers and nanoscale inorganic fillers. It is claimed that [15] this area of research is opening pathways for engineering flexible composites that exhibit advanced mechanical, thermal, optical

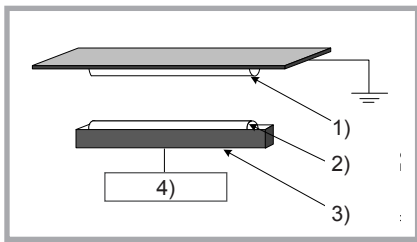


Figure 1. Schematic view of the electrospinning technique used for the production of nanocomposites; 1) upper electrode, 2) lower electrode (rotating cylinder), 3) tray with polymer solution, 4) power supply.

and electrical properties compared with conventional composites [14, 15].

In our clinical environment there is a common call for the prevention of microbial adhesion and biofilm formation as they may have serious implications – irritation, inflammation, etc. It is well known that infections adversely affect wound repair through ongoing chronic inflammation as well as production of toxic molecules and metabolites from both the microbe and immune response. Thus the insertion of nanoparticles (carbon nanotubes, metals and their oxides, etc.) into macro- and micro-sized polymeric matrices for the improvement of antimicrobial properties is currently under intensive research, during which patient conditions are monitored [2, 14, 16 - 18].

Silver is widely used not only due to its superior optical, electrical and catalytic properties, but also because it is a non-specific antimicrobial, acting against a very broad spectrum of bacterial, yeast and fungal species likely to contaminate wounds and body cavities. This ac-

tion derives from the binding of positive silver ions with the negatively charged microbial proteins preventing their replication. Silver is also active on biofilms, critically challenging foreign bodies embedded. Different additives are being used as a constituent of conventional (in the range of micrometers) fibres, but nanocomposites are still under investigation [18 - 20].

The aim of our research was to embed metal (at the first stage of our research – Cu) nanoparticles into a nanofibrous structure using a quite different technique – a rotating drum immersed in a polymer solution instead of a syringe. Cu nanoparticles, affected by the strong electrostatic field between the electrodes (the direction of the field in the electrospinning device was directed upwards), could diverge from the polymer solution. At the beginning of the research, Cu nanoparticles were used as Cu properties are quite similar to those of silver (not to mention antibacterial ones); besides, Cu is much cheaper. As a matrix material for the production of nanofibres, poly(vinyl alcohol) (PVA) was chosen as it is widely used in many areas, including medicine.

Experimental

Polyvinylalcohol (PVA) nonwovens containing Cu nanoparticles were produced at Kaunas University of Technology, Faculty of Design and Technologies, Department of Textile Technology (Lithuania).

Water based 8 wt% PVA (molecular weight – 70,000 g/mol, degree of hydroly-

sis 88%) solution was prepared, and then 1 wt% of Cu nanoparticles of 40 ± 5 nm size (specific surface area 15 ± 5 m²/g) were added (nanoparticles were purchased from the company ‘PlasmaChem’). Nanofibres were formed in an environment of ambient temperature and humidity (19 °C and 60%, respectively) using an electrospinning device – ‘Nanospider™’, presented in Figure 1 (for an exhaustive description of the technique see [12]). The producer of this electrospinning equipment is Elmarco, Czech Republic. For the initial part of our research, a distance between electrodes of 16 cm and 65 kV voltage were randomly applied.

During the electrospinning process, water from the solution evaporated and polymeric nanofibres solidified. For visual and quantitative evaluation, the samples produced were analysed using a scanning electron microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) at the Institute of Metals and Technology (Slovenia).

In order to obtain good quality SEM images, the samples prepared were carbon coated up to 4 nm in thickness using a Gatan PECS 682 to provide conductivity.

For measurement of the average diameter of the nanofibres and for evaluation of the presence of single Cu particles or their clusters on the surface of the nanoweb, secondary electron images (SE image) were obtained using an FEG SEM Joel JSM 6500F.

In order to evaluate if there were Cu nanoparticles inside the nanofibres, the

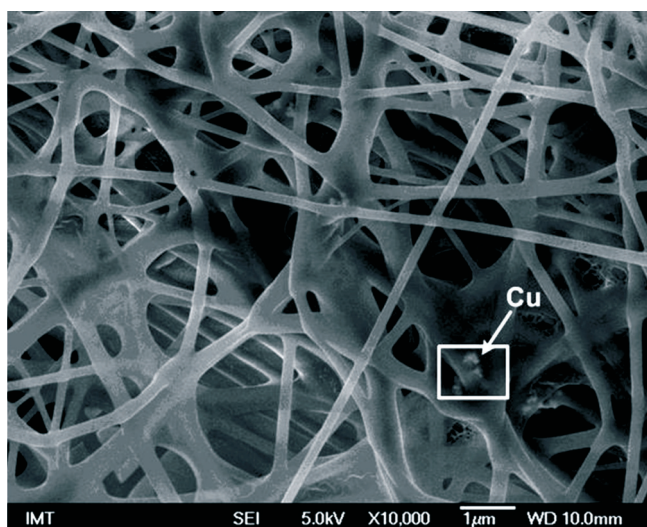


Figure 2. SE image of PVA nanofibrous web, containing cluster of Cu nanoparticles.

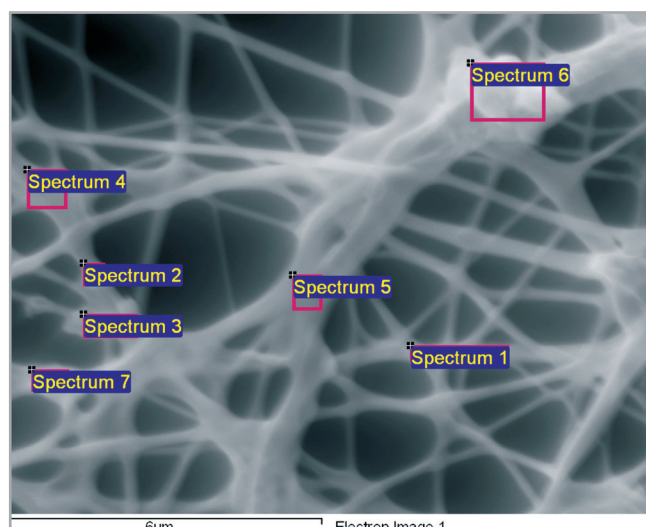


Figure 3. Areas of X-ray microanalysis performed.

samples were also analysed using Energy Dispersive X-ray Spectroscopy (EDS) in the form of an INCA X-SIGHT LN2 with Inca Energy 450 software. Analysis was performed using a primary electron beam of 5 kV accelerating voltage and probe current of 0.8 nA.

Several SEM images of the samples were made, and the average diameters (excluding obviously cohered ones formed during the movement of the PVA solution towards the collector) of the nanofibres were measured using the Image Analysis System Lucia 5.0 (see [21]), which allows to do precise visual measurements (precision is down to 10 $\mu\text{m}/\text{pixel}$) at an average magnification of 10,000).

Results

The average diameter of the nanofibres was 217 nm and the coefficient of variation 8.2%, which is quite a low value, especially considering that the production process of a nonwoven nanofibrous material is hard to control. It is well known that when moving between the electrodes, some filaments do conglutinate, thus resulting in much thicker filaments, thus they were not taken into account.

In some SEM pictures, clusters of different sizes of Cu nanoparticles can be clearly seen (*Figure 2*). In the nanowebs obtained there were no Cu nanoparticles stuck onto the surface of the fibres – all of them were coated by polymer film.

A sample of an SE image for which an EDS analysis was performed is presented in *Figure 3*. It is well known that the smallest amount of particles that can be detected using EDS is 0.1%, thus the results do present reliable information about the distribution of small amounts of Cu in a nanoweb. Analysis was made at several randomly chosen points where clusters of solid nanoparticles could not be seen in SEM pictures. Fibres of different diameter were chosen for this purpose.

Results of the EDS analysis performed in weight% and in atomic% are presented in *Tables 1* and *2*, respectively. Representative spectra are shown in *Figures 4 & 5*, and for clarity only two spectra (spectra 1 and 6) were randomly chosen and presented in this paper. This does not represent the full chemical analysis since it is impossible to detect hydrogen by EDS. The peak of hydrogen is not visible because the first element of the periodic

Table 1. Percentage content of the particular elements, results of X-ray microanalysis performed in weight %, for areas indicated in *Figure 3*.

Element	Spectrum							Mean value
	1	2	3	4	5	6	7	
Carbon	65.47	68.86	68.95	70.62	74.45	38.83	67.78	65.00
Oxygen	17.27	15.88	16.77	16.02	16.72	17.79	15.57	16.58
Copper	7.08	5.04	4.15	4.24	1.73	23.73	4.66	7.23

Table 2. Percentage content of the particular elements, results of X-ray microanalysis performed in atomic %, for areas indicated in *Figure 3*.

Element	Spectrum							Mean value
	1	2	3	4	5	6	7	
Carbon	78.33	80.37	80.03	81.40	82.81	60.49	79.89	77.62
Oxygen	15.52	13.92	14.61	13.86	13.96	20.80	13.77	15.21
Copper	1.60	1.11	0.91	0.92	0.36	6.99	1.04	1.85

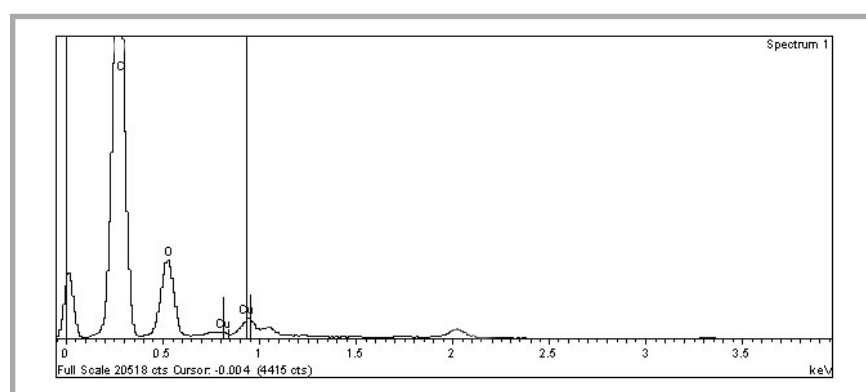


Figure 4. EDS spectrum 1, mean peaks are labeled.

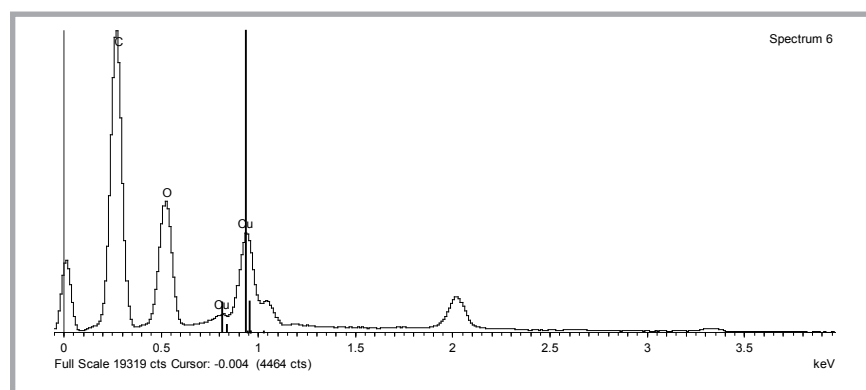


Figure 5. EDS spectrum 6, mean peaks are labeled.

table that can be analysed or detected by the EDS method is Be. Such elements as H and He have insufficient electrons to generate X-rays, and other elements up to Be have low-photon energy and due to the absorption in the detector window, the efficiency of the detector is too low. Such elements as H, He, Li are too light to be detected - their X-rays are stopped in the detector window).

The results of mapping Cu nanoparticles in the nanoweb produced are presented in *Figure 7* (see page 20). White dots show

Cu nanoparticles that are inside nanofibres (not seen in SE pictures).

It is clearly visible that the distribution of Cu nanoparticles in different places of the nonwoven material is not even; however, it can be explained by the noneven distribution of Cu nanoparticles both in the solution (because of randomly oriented polymeric chains) and in nanofibres, because the structure of the nonwoven material is not even.

All the results presented above show the possibility of incorporating Cu na-

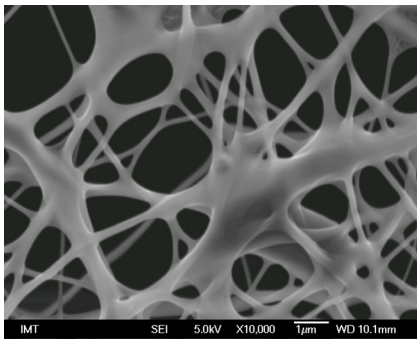


Figure 6. SE image of PVA nanoweb containing Cu nanoparticles.

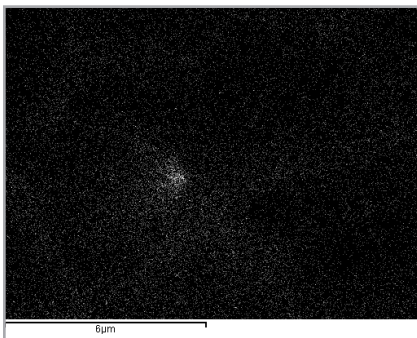


Figure 7. Mapping of the same sample, presented in Figure 6: Cu nanoparticles (white dots) in a produced nanoweb.

nanoparticles into the internal structure of nanofibres via this innovative technique. EDS analysis and individual SE images confirm that metal nanoparticles are distributed in the structure.

In **Figures 4** and **5**, peaks indicating the presence of carbon, oxygen and Cu are clearly seen. The greatest amount is of carbon – the main constituent of PVA, followed by oxygen and Cu. In **Figure 5**, the amount of Cu is significantly greater than in **Figure 4**, which can be explained by the thicker filament; thus the concentration of Cu nanoparticles there is greater as well.

In **Figure 6** (see page 20), an SE image of a PVA nanoweb containing Cu nanoparticles is presented, and the results of the X-ray mapping of Cu nanoparticles of the same sample are presented in **Figure 7** (see page 20).

Using EDS, different chemical elements can be detected in the structure being analysed. In **Figure 7**, the region containing Cu nanoparticles (white dots), the same region that is presented in **Figure 6** can be clearly seen. In general the distribution of nanoparticles is quite uniform, which means that despite the fact that it not really possible to control

the distribution of metal nanoparticles in a polymer solution, it is still feasible to produce a nanocomposite to incorporate Cu nanoparticles into nanofibres without any special additives using common parameters of the electrospinning process. Future research will be carried out using Ag nanoparticles. Furthermore, the preparation of polymer solution and parameters for the production of nanocomposites will be analysed and improved in order to avoid the formation of clusters of any size in the structure of a nonwoven material.

Conclusions

1. Despite the strong electric field (65 kV and more) between the electrodes of the electrospinning device (which was used in the production of the samples), it is possible to insert metal nanoparticles into the fibres comprising the nanoweb, although both the polymer and nanoparticles move upwards.
2. The distribution of metal nanoparticles is not uniform, but it can be explained by the unevenness of nonwoven material, as well as by the random distribution of nanoparticles in polymer solution.
3. The possibility of inserting different types of metal nanoparticles in a polymeric nanostructure may lead to great opportunities of using such structures in many fields: the production of electroconductive materials, antiseptic wound dressings, implants, etc.

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