DUAL EFFECT OF CuO PARTICLES ON ELECTROSPINNING PROCESS AND PROPERTIES OF POLYURETHANE NANOFIBERS

Ganna UNGUR, Jakub Hruža

Technical university of Liberec, Studentska 1402/2, Ganna.Ungur@tul.cz, jakubhruza1@seznam.cz

Abstract

In the present research work polyurethane (PU) nanofibers with different concentrations (0.5; 1; 5%) of CuO particles by electrospinning according Nanospider technology in the form of roll electrode against flat electrode. CuO particles were introduced into the polymers solution before fiberforming. The effect of catalysts on the viscosity of solutions was recorded only for a concentration 5%. SEM results confirmed well oriented nanofibers and good distribution of CuO particles. Average index of surface density for samples of pure PU fibers 2.8 g/m², for PU/CuO(5%) is 12,257 g/m². So particles of CuO promote to the proces sof electrospinning and increase its performance due a conductive properties of copper. The microorganisms Escherichia coli and Staphylococcus aureus have been used to determine the antimicrobial efficiency of these samples. Good bactericidal prolongation effect was indicated for prepared nanofibers. Efficiency of the filtration properties was measured for pure PU and modified samples. All samples demonstrated filtration efficiency higher than 99% and it means that deposition of nanoparticles didn’t decrease filtration properties. Consequently, the particles of CuO have the dual effect on the producing of PU nanofibers, improving performance and giving antibacterial properties. So obtained fibers can be used as a filtration materials with good antimicrobial properties for the climatization systems.

Key words: polyurethane nanofibers, electrospinning, filtration, antibacterial properties.

1. INTRODUCTION

The history of filtration has, in some way, reflected the history of human needs. At the present time the necessity for clean air exists along with the necessity for a large number of industrial processes; and certain parts of industry itself rely on clean air of exceptional quality. The medical and biological fields rely on sterile air; and filtration can also improve air quality in the offices, houses and in transport of all types. [1] As the efficiency of particle capture in an air filter increases with decreasing fiber diameter in a mat, using nanofibers filters for air or gas filtration as well as in liquid filtration are effective application. Electrostatic spinning or electrospinning is the most convenient and scalable technique for nanofibers production. [2] This technique typically involves a solution stretching process in which the polymer solution driven by a strong electric field is stretched rapidly into dry or semidry fibers and deposited directly onto a collector, usually in the form of nonwoven fiber mat. [3] In this work we used Nanospider method to obtain polyurethane nanofibers. Nanospider is the unique method which has been used in industry to produce nanofibers continuously. This method was invented by O.Jirsak in Technical university of Liberec, 2003. Also this method is the first all over the world, which was commercialized under the name of Nanospider from Elmarco Company in Liberec. [4]

There is more than 1.8 thousand species of bacteria and microbes in the air. These are results of research conducted by the National Laboratory, Berkeley. Air pollution by microbes comes from soil, animals, humans and plants. Bacterial spores, fungi, yeast and various micrococcus could be in the air. Ambient air may be a factor of transmission for respiratory viral infections, influenza, tuberculosis, diphtheria, staph infection, etc. Microbial contamination of air is greatly reduced by the good work of ventilation, the presence of antibacterial filters for supply air. [5]
CuO nanoparticles are very efficient in imparting antibacterial effect to fabric. Copper oxide plated or impregnated synthetic fibers possess broad spectrum biocidal properties: they are antibacterial, antifungal, antiviral, and they kill dust mites. [6]

Polyurethanes are one of the most widely used polymers in biomedical, filtration, protective clothes, composites, sensor and wound heating application. [3] So in present study PU nanofibers with CuO particles in polymer matrix has been produced by using Nanospider technique. The effect of CuO on the properties of PU solution and on the surface density of finished fibers was investigated. Antimicrobial activities and filtration properties have been evaluated. According our results, the prepared nanofibers containing particles of CuO could be employed as antibacterial filters in the modern climatization and ventilation systems and for many biological applications.

2. EXPERIMENTAL WORK

2.1 Materials

In this work, polyurethane (Larithane LS 1086, aliphatic elastomer based on 2000g/mol, linear polycarbonated diol, isophorone diisocyanate and extended isophorone diamine), was used as a polymer. The solution was prepared at 15 wt% concentration with dimethylformamide (DMF) solvent. For checking antimicrobial activity microbial strains Escherichia coli and Staphylococcus aureus, purchased from the Czech Collection of Microorganisms (Masaryk University in Brno), were used as model organisms. Incubation was performed in a sterile blood agar (Columbia agar) from company BIO-RAD.

2.2 Methods

Different concentration of CuO (0.5; 1; 5%) were added to the solution of PU. These systems were mixed on the magnetic stirrers for 12 hours. Solution properties such as viscosity and conductivity were determined. Conductivity was measured by a conductivity meter (Radelkis, OK-102/1); rheological properties of solutions were measured using Rheometer HAAKE Roto Visco 1 at 23°C.

Roller spinning method (Nanospider) with high voltage power supply was used to produce nanofibers (Fig. 1).

![Fig.1: (a) Schematic diagram of Nanospider method and (b) the rotating cylinder.](image-url)
Nanospider consists of rotating cylinder to spin fibers directly from the polymer solution. The PU polymer solution with particles was filled into a polypropylene dish and the bottom of aluminum rotating cylinder body with spikes is partially immersed into the polymer solution. High voltage is connected to the rotating roller. The collector electrode is usually grounded to create potential difference (Fig.1(a)). As the solvent evaporates, the jets of polymer solution are transformed and the solid nanofibers are obtained before reaching to the collector electrode. The nanofibers were collected on polypropylene (PP) spunbond nonwoven antistatic material.

The fibers and particles morphology and diameters were determined with a scanning electron microscopy (SEM). Average diameters of fibers and particles were calculated from the SEM photos using Lucie 32G computer soft ware. The surface density of prepared samples with different concentrations of CuO was found.

2.3 Antimicrobial test
Analysis of antimicrobial test was carried out by making samples from pure PU nanofibers and CuO containing nanofibers. Two different testing methods were used for the estimation of antibacterial characteristics of produced materials. First test was NORMA (qualitative assessment). Tests were performed according to EN ISO 20645 – Textile fabrics – detection of antibacterial activity – test spread agar plate. The samples were sterilized for 20 minutes at 90°C. Bacteriological inoculums (concentration $10^5$CFU in volume 1 ml) were vaccinated to the Petri plates with blood agar. Tests samples were placed to the centre of the plate with bacteriological inoculums. Then plates were placed to the thermostat and incubated for 24 hours at 36.5°C. The results were photographed and counted. The second test was NORMA (quantitative evaluation of the number of bacteria updated again). Samples of size 18×18 were sterilized for 20 minutes at 90°C. Sterilized samples were placed in sterile containers and vaccinated bacterial inoculums in a concentration $10^5$CFU in 0.1 ml of bacterial inoculums. The containers were placed to the thermostat and cultured at 36.5°C for 24h. After 24h of incubation 100 ml of saline solution were added to the containers, thereby diluting the bacteria was adjusted to $10^3$CFU. Containers were vortexing for 5min. 1ml of bacteriological media was removed from each container and vaccinated to the Petri plate with blood agar. Plates were placed to the thermostat and incubated for 24h at 36.5°C. Then the results were photographed and counted.

2.4 Efficiency of the filtration
Filtration efficiency of pure PU nanofibers and nanofibers with CuO particles was measured on the Sodium Chloride aerosol test equipment (Bench Mounting Rig type 1100P). This device can measure filter efficiency, pressure drop and impact air flow according to standards: BS 4400 (Method for Sodium Chloride Particulate Test for Respirator Filters-British standard), EN 149 and EN 143 (Respiratory Protective Devices- European standards). The device is possible to use for testing a high efficiency filters such as a HEPA filters. It is possible to estimate classes according to test standards: ASHRAE 52.2, EN 779 and EN 1822. Parameters: test particles: NaCl; particle size: 0,002 – 2 µm, mean value of particle size: 0,6 µm; particle concentration: up to 13 mg/m³; air flow: 10 – 95 l/min, air velocity 1 - 9,5 m/min; test sample size: 100 cm²; filter sample thickness: up to 40 mm.

3. RESULTS AND DISCUSSION

3.1 Determination of the polymer solution properties
Since obtained samples with different concentrations of CuO showed different surface densities, we decided to check the possibility of the influence of used catalyst on the conductivity of PU solutions (Tab.1). We found that increasing of CuO concentration had no significant effect on the conductivity if the solutions.
is easily explained by the fact that between the copper oxide and PU solution cannot occur any chemicals bonding. Therefore, increasing of the fiber’s surface area with increasing concentration of the catalyst can be explained by the fact that the conductive properties of copper is manifested directly in contact CuO containing solutions with the surface of the charged cylinder in electrospinning process.

### Tab.2: The changing of conductivity with increasing of CuO concentration

<table>
<thead>
<tr>
<th>Concentration of CuO (%)</th>
<th>Conductivity of solution (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.8</td>
</tr>
<tr>
<td>0.5</td>
<td>2.82</td>
</tr>
<tr>
<td>1</td>
<td>2.82</td>
</tr>
<tr>
<td>5</td>
<td>2.84</td>
</tr>
</tbody>
</table>

Viscosity measurements showed that increasing the concentration of CuO leads to the higher viscosities (Fig.2). However, it was not reflected in the deterioration of the solutions spinnability. In the fiberforming process with growth of concentration was recorded increasing the number of Taylor cones. Fiber diameters did not rise significantly with rising of concentration.

![Fig. 2: The variation of viscosity (f in Pas) with shear rate (Á in 1/s) for PU solutions with different concentrations of CuO](image)

### 3.2 Characterization of the producing material

The surface density of fiber layers for different concentration of CuO was calculated. According obtained data we have surface density for pure PU = 2.8 g/m², PU/CuO(0.5%) = 4.67 g/m², PU/CuO(1%) = 6.45 g/m², PU/CuO = 12, 28 g/m². On the basis of these data we can suggest that copper oxide contributes to the process by electrospinning due a conductive properties of copper. Through SEM images (Fig.3) it was found that a lot of particles of CuO of different sizes are on the surface and in the volume of PUR nanofibers. After electrospinning visible changes of color were noticed between pure and containing copper oxide fibers. Nanofibers mats with CuO exhibited brown color, compared to pure PU layer which retained its original white color. The brightness of color was depending on CuO content.

The use of copper oxide at electrospinning affects the small increase in the diameter of fibers and particles with increasing the concentration of modifier, but there is no expansion of the distribution of diameters (Tab.2).
Fig. 3: SEM images of nanofibers that contain different amounts of CuO.

Tab. 2 Diameters of PU fibers and particles of CuO on the fibers surface

<table>
<thead>
<tr>
<th>Concentration of CuO (%)</th>
<th>Fibers diameter distribution (nm)</th>
<th>Average fiber’s diameter (nm)</th>
<th>Particles diameter distribution (nm)</th>
<th>Average particle’s diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80-300</td>
<td>156</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>100-290</td>
<td>187</td>
<td>20-240</td>
<td>127</td>
</tr>
<tr>
<td>1</td>
<td>100-300</td>
<td>189</td>
<td>20-312</td>
<td>139</td>
</tr>
<tr>
<td>5</td>
<td>120-320</td>
<td>190</td>
<td>50-350</td>
<td>165</td>
</tr>
</tbody>
</table>

3.3 Antibacterial properties

According first testing method for samples with different CuO concentrations and pure PU fibers (standard) we found that standard sample showed limit antibacterial effect (inhibition zone = 0), PU/CuO 0.5%, 1% and 5% - very well antibacterial effect (inhibition zone > 1mm) to both microbial strains Escherichia coli and Staphylococcus aureus (Fig. 4).

Fig. 4: Photo of testing samples with Staphylococcus aureus.

According second testing method in the bacterial strain E. coli the standard sample has a visible sign of antibacterial effect. It is clear that the substrate itself shows antibacterial properties. Number of again renewed bacterial colonies is approaching 500. For PU/CuO 0.5% is visible one bacterial colony, so antibacterial efficiency is 99.9%. It is an excellent effect. There have been no bacterial colonies for PU/CuO 1% and 5%, so antibacterial activity is 100%.
Second testing method in the bacterial strain St. aureus showed visible growth of bacteria in the entire area for standard sample, so it has no antibacterial effect. PU/CuO 0.5% and 1% have 99.9% of antibacterial efficiency. The best result was for PU/CuO 5%. It appeared 100% of antibacterial activity. Then we checked whether the samples with CuO exhibit antibacterial efficiency continuously. For to find out this, the samples were washed by water under constant pressure for four hours. After washing tests for antibacterial properties were repeated. The results of repeating test have shown that PU nanofibers with 0.5% of CuO have antibacterial efficiency 94%, with 1% - efficiency 95.2%, with 5% - 97.7% efficiency. So prepared materials have been demonstrated prolongation effect of antibacterial activity.

3.4 Efficiency if the filtration (E)
Pure PU samples has shown average E = 99.96%; for PU/CuO 5% E = 99.73%. These data show us that the presence of particles does not adversely impact on the excellent properties of polyurethane nanofibers.

CONCLUSIONS
The result of our work is PU nanofibers modified by particles of CuO. We found that PU/CuO colloidal solution can be easily electrospun to form smooth nanofibers. The copper oxide particles were found to have a spherical morphology and well dispersed on PU nanofibers. Modified fibers have very high surface density in comparison with pure fibers, indicating the beneficial effect of copper on the course of the process of electrospinning. The use of catalyst has no negative impact on the excellent filtration properties of PU nanofibers. Producing materials demonstrated high antibacterial effect (about 100%). Prolongation effect of antibacterial properties in time was tested by washing with water under pressure for 4 hours. The fibers with 5% CuO preserved the effectiveness of antibacterial action 97.7%. So CuO showed the dual effect on the producing polyurethane nanofibers, increasing surface density of fiber layers and giving antibacterial properties. Our samples could be used as filter materials with antibacterial action for modern systems of indoor air cleaning.

ACKNOWLEDGMENT
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LITERATURE