ELECTROSPINNING AND ELECTROSPRAYING OF POLYMER SOLUTIONS WITH SPHERICAL FULLERENES

Eva KOŠŤÁKOVÁ, Eva ZEMANOVÁ, Petr MIKES, Julie SOUKUPOVÁ, Hana MATHEISOVÁ, Karel KLOUDA

Technical University of Liberec, Studentska 2, 460 01 Liberec, Czech Republic, EU, eva.kostakova@tul.cz, petr.mikes@tul.cz

State Office for Nuclear Safety, Senovazne namesti 9, 110 00 Praha 1, Czech Republic, EU, eva.zemanova@sujb.cz, karel.klouda@sujb.cz

Fire rescue service of Czech republic, Piskova 42, Praha 4

Abstract

Electrospinning and electrospaying are two similar technologies which differ mainly in the structure of produced materials. Final products of electrospinning are nanofibers, however the electrospraying results are spherical bodies - microparticles deposited onto support material. It is the way how to create composite material made of three or four different substances. The article explains production of composite nanofibers with incorporated spherical hydroxylated fullerene C60oxi and production of spherical bodies with C60(OH)x by electrospraying technology. Needle-less method is used for both described technologies that require focusing on the uniform distribution of nanoparticles (fullerenes) inside a polymer solution. The nanofibrous materials (based mainly on PVA/water solutions) structure characteristics are tested and there are also presented results from TGA analysis, which show that the increasing fullerene amount inside nanofiber increases the thermal resistivity of them. The limit amount of fullerenes inside the polymer solution, which allows to electrospun by needle-less electrospinning technology is presented. The ethanol solution of PVP was used as a shell polymer for encapsulation of fullerenes by electrospraying technology. Choice of the solvent plays the crucial role for creation of submicron droplets. There is almost no limitation of amount of encapsulated particles into the matrix. Scanning electron images of several different samples will be presented (including different support materials - nonwovens, nanofibrous materials etc.).

Keywords: Fullerene C60, hydroxylated C60, electrospinning, electrospraying, nanofibers, TGA

1. INTRODUCTION

Electrospinning and electrospaying are "sister" technologies of polymer based nanomaterials production. Almost the same devices and arrangements are used for both of these technologies. Although final products are different and can be used separately or together. The main products of electrospinning are nanofibers. Nanofibers and nanofibrous layers are used in wide range of application [1] nowadays. Nanobeads as a product of electrospaying can be used mainly in medicine or special filtration. The nanofibers and nanobeads can be produced from pure polymer material or there can use another material as an additive. One of such materials can be spherical fullerenes, which bring its special properties. Such composite nanomaterials can finally achieve better properties with minimal weight or surface changes. Needle or needle-less technologies have been used for both, electrospinning and electrospraying. Presently, the most of electrospinning or electrospaying techniques used for production such nanomaterials is based on capillary electrospinning - needle electrospaying. On the other hand, especially needle-less electrospinning is used for mass production of these nanomaterials mainly nanofibers. The electrospinning from free surface (or almost free surface) of liquid was named as a needleless electrospinning by Yarin [2]. However before that, the needleless modification for continuous production of nanofibers was patented [3, 4]. A polymer solution is for spinning supplied into the electric field using a surface of a rotating charged
cylindrical electrode. Thus no syringes, capillaries, nozzles or needles are needed. The main advantages of the technology are: (i) continuous mass production, (ii) high production capacity and (iii) ease of upkeep.

The most of devices mainly constructed for nanofibers production can be also used for electrospraying and thus for production of nanobeads. There is also possible to employ two these devices and combine nanofibers and nanobeads in one material together.

Spherical fullerenes mainly C60 as the most stable form of fullerene are very popular in many research fields. Nowadays only several publications about problematic dealing with production of composite electrospun nanofibers with integrated fullerene can be found [5, 6]. Different derivatives of C60 are used because of their different surface properties (energies), what corresponding with different "willingness" to be well dispersed in different solvents. There is generally known pure C60 is hydrophobic material. This is why oxiderivatives are used in water dispersion as in the study presented here. The fullerene oxiderivative allow creating of its better dispersion in water thanks to hydrophilic OH groups on the fullerene surface.

2. EXPERIMENTAL SECTION

The needle-less electrospinning technology was used for the production of nanomaterials here. Nanofibers with and without spherical fullerenes and nanobeads as a product of electrospraying with and without derivative fullerenes were produced. The derivative C60 was prepared using peracetic acid and subsequent hydrolysis (follow only “C60oxi”) according to the method that we described in [7, 8]. Scanning electron microscope (Phenom, FEI and Zeiss) was used for visualization of produced nanofibers and nanobeads and Raman spectroscopy (Horiba JOBIN Yvon – LabRam IR with Olympus BX41 with area of measuring point was in 1,2 μm in diameter) for composition of nanoparticles (nanofibers and nanobeads) analysis.

2.1 Electrospinning

The polyvinylalcohol (PVA, Mowiol 18-88, average mol wt 130.000 from Kuraray) water solution 10 wt.% with crosslinking agents (4 wt.% of 40 wt.% glyoxal solution and 3 wt.% of 85 wt.% phosphoric acid solution from dry PVA content) were electrospun and subsequently crosslinked at 135°C for 5 minutes. The material was used as a control sample. Then PVA nanofibers with addition of 1, 2 and 3 wt.% of C60oxi where produced. Used voltage for electrospinning was 20-25kV. After electrospinning the same crosslinking process as for the control sample was used. Couptiss Ultra Sons HS30 with power 30 W and frequency 30 kHz (Calemard, France) was applied for 60 seconds for dispersion of fullerenes inside the water. The final structure of electrospun nanofibers can be seen in Fig.1.
The diameters of nanofibers measured by image analysis are: control sample 210±56 nm; 1 wt.% C60oxi 214±73 nm; 2 wt.% C60oxi 219±74 nm; 3 wt.% C60oxi 224±72 nm.

A change of thermal stability of the produced nanofibrous materials was assessed at Fire rescue service of Czech Republic, by means of TGA and TG-DSC methods. Measurements of weight loss and relaxed-consumed thermal energy depending on used temperature and time are principles of these methods. The tests were performed according to accredited methods, apparatus STA 1500 THASS. The graphical results are presented in Fig.2. Peak area is directly proportional to the heat freed or consumed in the reaction and the height of the peak is directly proportional to the rate of reaction. The obtained results clearly show that adding fullerenes into nanofibers has led to an increase in thermal resistance. The thermal analysis showed that the addition of fullerene always increases the beginning thermal decomposition temperature. As it is visible in Fig.2, all materials exhibit significant exothermic process. This process begins at 220°C for control sample, at 235°C for sample PVA with 1 wt.% of C60oxi, at 450°C for PVA with 2 and 3 wt.% of C60oxi.

![Graphs presented behaviour of nanofibrous samples with different amount of C60oxi under increasing temperature.](image)

The inhibitory effect of fullerene C60oxi was clearly detected during the thermo-oxidative degradation of composite nanofibers based on PVA. This effect is disproportionately increased with increasing C60oxi concentration inside electrospun nanofibers.

2.2 Electrospaying

Water solutions are not very suitable for electrospaying due to the high surface tension of the solvent. According experience the ethanol was chosen, mainly because its health safety and relatively low cost. Thus the solution of polyvinylpyrrolidone (PVP, average mol wt 40.000 from Sigma) in ethanol was electrosprayed. The tested concentrations were from 1 to 10 wt.%. Finally 5 wt.% was found as optimal concentration for
electrospraying. The product had the most uniform size of droplets - beads and no fibers were created. When the higher concentration was used the nanofibers with beads started to be visible on the support material. The concentration 10 wt% is the optimal concentration for electrospinning of solution PVP in ethanol. Solution of 5 wt% PVP in ethanol with addition of 1, 2 and 3 wt% of C60oxi was electrospayed. The sonication was applied for better dispersion of fullerenes inside the solution. All of these samples were successfully electrosprayed by needle-less electrospinning method onto spun-laced nonwoven support material. The support material consists of viscose fibers, thus scanning electron images presenting nanobeads as a product of electrospraying onto viscose fibers (see Fig. 3). There is necessary to admit higher concentration of C60oxi, but it does not mean significant change of average beads diameter or standard deviation. Raman spectroscopy proofs the fullerene presence inside the produced materials.

**Fig. 3** Scanning electron microscope images of PVP electrosprayed beads: pure PVP on the left (average diameter of beads - 427±190 nm), PVP with 2 wt% of C60oxi on the right (415±175 nm). The upper images presented electrospraying onto viscose fibers – spunlaced nonwoven and the bottom electrosprayed beads onto a paper.

3. **CONCLUSIONS**  
The presented study showed that the composite polymer composite nanomaterials (electrospun nanofibers and nanobeads as a product of electrospraying) can be produced at the same device without any changes of the process conditions. There is only necessary to find optimal concentrations and set up the material
conditions, solution properties respectively. There was also confirming that it is possible to electrospin or electrospray composite nanomaterials with addition of spherical fullerenes, when the solution preparation and fullerenes dispersion has the right conditions and procedure control. The combination of both or these technologies for production materials containing nanofibers and also nanobeads was prepared and such materials are tested nowadays.

AKNOWLEDGEMENT

The main support for this research was provided by The Ministry of Interior of the Czech Republic, program BV II/2-VS; grant No. 1656, “Nanomaterials to persons protection against CBRN substances” and grant PID: VG2VS/112, “Applied research of new generation protective masks with nanofilters to increase men protection from design, technological and material point of view”. The authors also thank to Pavel Kejzlar from Laboratory of Analytical Methods, Institute of Nanomaterials, Advanced Technology and Innovations, Technical University of Liberec.

LITERATURE