

Fullerene C60 and its derivatives as nanocomposites in polymer nanofibres

Eva ZEMANOVÁ¹, Eva KOŠŤÁKOVÁ², Karel KLOUDA¹

¹State Office for Nuclear Safety, Senovazne namesti 9, 110 00 Praha 1, Czech Republic, EU

²Technical University of Liberec, Studentska 2, 460 01 Liberec, Czech Republic, EU

Email address:

eva.zemanova@sujb.cz(E. ZEMANOVÁ), eva.kostakova@tul.cz(E. KOŠŤÁKOVÁ), karel.klouda@sujb.cz(K. KLOUDA)

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Abstract: This work describes the application of oxo-derivatives of fullerene C60 and pristine fullerene as a nanocomposite in polymeric nanofibres. In this work we used oxo- fullerene derivative, of which preparation was presented by the authors of the State office for nuclear safety (Prague) on Nanocon 2009 and on Nanocon 2010 [1, 2]; there was presented its application in vivo as a radioprotective agents. With respect to wide spectrum of potential utilization of unique chemical, structural and electron properties of fullerene we investigate its another possible technical application as nanocomposite in polymer nanofibres. The nanocomposite polymer nanofibers were produced by needle-less electrospinning method. Polyvinyl alcohol, polyurethane and polyvinyl butyrate were used as polymers. Thermal resistance of obtained nanofibres with and without nanocomposites was tested by simultaneous thermogravimetric analysis and differential thermal analysis (TGA/DTA). The retarding influence of fullerene and its derivative on the course of the thermal decomposition of nanofibres is discussed.

Keywords: Fullerene C60, Derivative of C60, Nanocomposites, Polymer Nanofibres, TGA, DTA

1. Introduction

Fullerenes C60, molecules composed of 60 carbon atoms in the form of hollow sphere, are very interesting and nowadays all over the world studied nanomaterial [3]. Fullerenes C60 can be also incorporated into other amazing nanomaterial – electrospun nanofibers. The production of such nanocomposite material where the matrix is presented by polymer nanofibers and “reinforcement” is presented by C60 is done by electrospinning technology. The technology uses electrostatic forces for self-organization of polymer solution/melt into a nanofibrous layer as is generally known [4]. Presently, the most of electrospinning techniques used for production of nanofibrous materials is based on capillary electrospinning. On the other hand, the electrospinning from free surface (or almost free surface) of liquid was named as a needleless electrospinning by Yarin [5]. However before that, the needleless modification for continuous production of nanofibers was patented [6, 7] and it is generally known as Nanospider™ technology now.

The materials originated thanks to connection of carbon nanoparticles (fullerenes or nanotubes) and electrospun

nanofibers are also in the center of the scientific researches, it is for example described in [4, 8-10]. Although the most of these publications presents nanofibrous materials electrospun from capillary electrospinning. A preparation of polymer solution with integrated nanoparticles C60 is fundamental for composite nanofibers production by needleless electrospinning. The solution preparation can be enhanced by ultrasound if it is necessary [9].

2. Electrospun Nanofibers Preparation

For the presenting contribution, there were chosen three different polymer materials as a matrix for fullerene and as “blind” samples. These polymers were polyvinyl alcohol (PVA, Slováké chemické závody, Mw approximately 60 000 g/mol; polymerization degree approximately 1100, 16 wt% water solution), polyurethane (PUR, Larithane LS1086 aliphatic elastomer based on 200g/mol, linear polycarbonated diol, isophorone diisocyanate and extended isophorone diamine, 30 wt% dimethylformamid solution), polyvinyl butyral (PVB, Kuraray, Mowital B60T, Mw approximately 60 000 g/mol). Polymer solutions described above were prepared from these polymers with and without

C60 and derivative C60 addition. The derivative C60 was prepared using peracetic acid and subsequent hydrolysis (follow only "C60oxi") according to the method that we described in [1, 2]. Electrospun by needleless electrospinning method was used. A distance between a grounded collector and a drop of the solution on the top of a charging metal cylinder was 10 cm. The surface density of all these samples was approximately 2 gm⁻¹. The nanofibrous layers were collected on spun-bond material for subsequent better separation.

Basic PVA water solution (10 wt.%) plus crosslinking agents (glyoxal 2,5 wt.% and phosphoric acid 2,5 wt.% of PVA) were electrospun and subsequently crosslinked at 140°C for 10 minutes. It was the "blind" sample. The basic PVA solution plus addition of water solution of 0,1 wt.% C60oxi was also prepared. Thus the final electrospun PVA nanofibers contain 1wt% of C60oxi. Used voltage for electrospinning was 23kV. After electrospinning was the same crosslinking process as for the blind sample. There

were used device Couptiss Ultra Sons HS30 with power 30 W and frequency 30 kHz (Calemard, France).

Basic PUR solution used for electrospinning of the blind sample had 10 wt.% in DMF. The basic PUR solution plus addition of 0,1 wt.% of C60 was also prepared. Thus the final electrospun PUR nanofibers contain 1wt% of C60. Solutions with C60 mixed one minute by sonication to completely separate agglomerates of nanotubes inside the solutions. Used voltage for electrospinning was 26kV.

Basic PVB solution used for electrospinning of the blind sample had 10 wt.% in acetic acid and ethanol in 1:2 ratio. The basic PVB solution plus addition of 0,1 wt.% C60oxi was also prepared. Thus the final electrospun PVB nanofibers contain 1wt% of C60oxi. Solution with C60oxi was mixed one minute by sonication to completely separate agglomerates of nanotubes inside the solutions. Used voltage for electrospinning was 22kV. Examples of produced nanofibrous materials are presented in Fig 1.

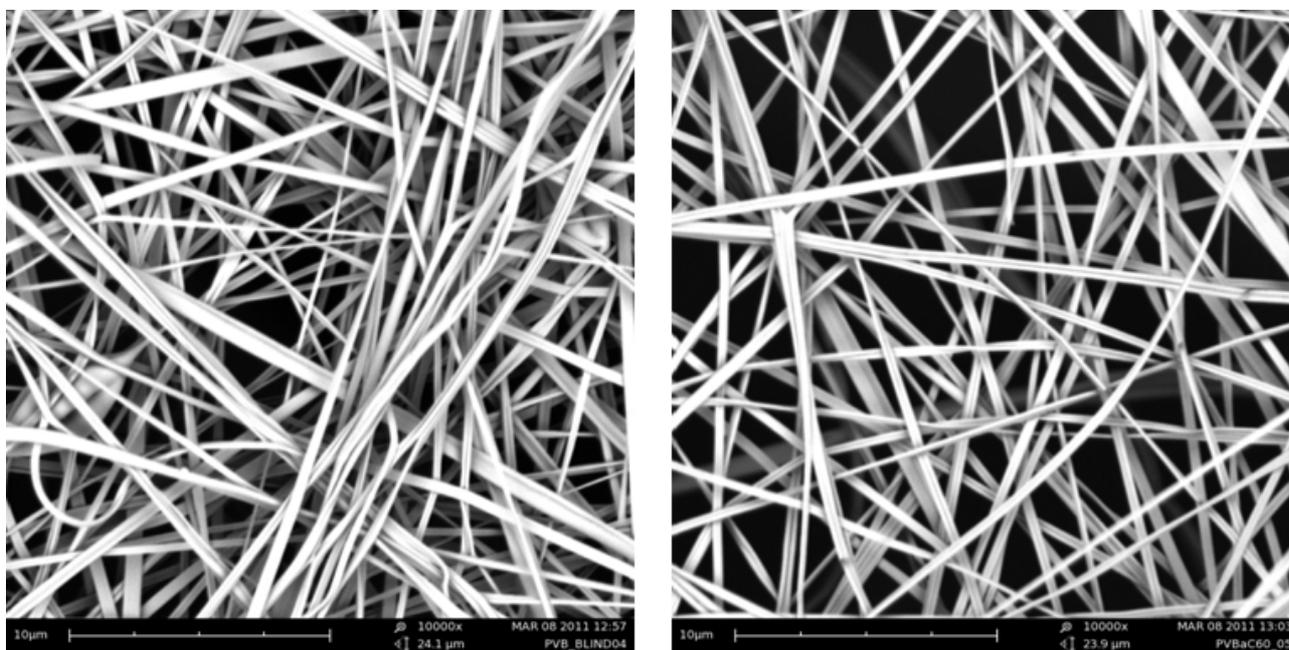


Fig 1. Scanning electron images of PVB electrospun nanofibers; blind sample on the left side and sample with C60oxi on the right side.

3. Measuring

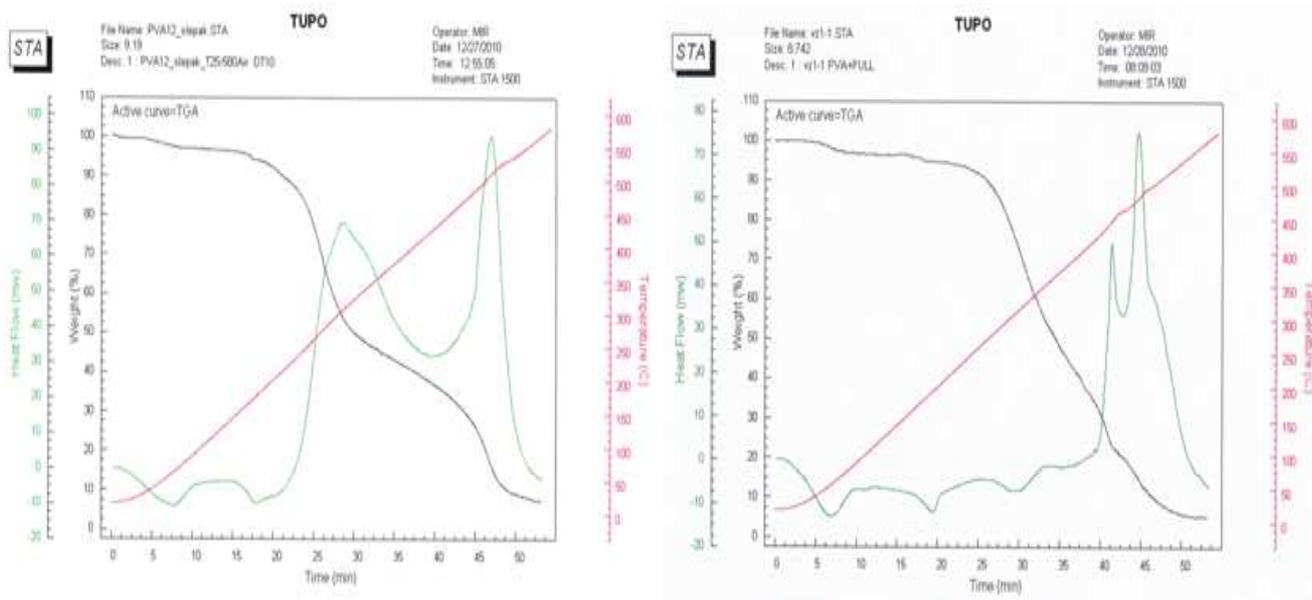
A change of thermal stability of the produced nanofibrous materials was assessed at Fire rescue service of Czech republic, by means of TGA and TG-DSC methods. These methods are based on measurements of weight loss and relaxed-consumed thermal energy depending on used temperature and time. The tests were performed according to accredited methods, apparatus STA 1500 THASS. The used degradation medium was air, used temperature regime went from 25°C to 550°C and sample-heating rate was 10°C/minute.

4. Conclusion

The results, which are listed in Table 1, showed that the samples with addition of C60oxi have significantly higher thermal resistance. A change of the thermal decomposition of nanofibers is evident from the curves of TGA and TG-DSC (see Fig 2) for nanofibers without and with addition of C60oxi. The main exoeffect characterizing thermal decomposition of PVA blind sample is suppressed after addition of C60oxi. Also the beginning of thermal decomposition shifted of 90°C. The polymer solution preparation before the electrospinning has an influence on thermal stability of final nanofibers. The result was shown mainly for PUR nanofibers with and without C60.

Table 1. Thermal characteristics of nanofibers based on PVA with and without C60oxi.

Material	The temperature of the sample weight loss start [°C]	Temperature maximum peak of the first exoeffect [°C]	Thermal decomposition of color (the first exoeffect/ total) [mW]
PVA (blind sample)	220	310	70/92
1. PVA - C ₆₀ Oxi (solution without crosslinking agents; fullerenes were mixed firstly only with water)	310	450	50/75
2. PVA - C ₆₀ Oxi (solution without crosslinking agents)	260	450	54/84
3. PVA - C ₆₀ Oxi (with crosslinking agents)	250	350	13/75

**Fig. 2** Thermal analysis graphs presenting blind sample of PVA nanofibers on the left side and PVA nanofibers with addition of C60oxi.

For the PVB nanocomposite - nanofibers with addition of C60oxi, thermal decomposition of color (exothermic reaction) was calculated from the TGA and TG-DSC measurements. The exothermic reaction was 20% higher for PVB blind sample in comparison with PVB nanofibers with C60oxi addition. Decomposition temperature is lower in PVB nanofibers blind sample (see Table 2).

The thermal testing of PUR nanofibers confirmed that the resulting effect (thermal resistance) of prepared composite nanofibers also depends on the method (polymer, solvent, nanoparticles, conditions and so on) of solution for electrospinning preparation. As it was mentioned before, dimethylformamid was used as a solvent for PUR for electrospinning. In one case, the fullerenes were incorporated into the final polymer solution (PUR and DMF) by ultrasound enhancement (see Table 2 – sample No. 4). In the second case, the fullerenes are mixed with DMF at first and then PUR is added (see Table 2 – sample No.5). The curves characterizing the decomposition by endoeffect (PUR without C60) and by exoeffect (PUR with C60) are shown in Fig 3. In the both cases, when PUR containing nanoparticles C60, the initial temperature of the decomposition increases.

Several alternatives polymer-fullerene bounds are

described in literature [3]. It is depending on the fact whether the fullerene reacts with a functional group of polymer chain additionally, or the fullerene molecule is a part of the polymerization process. A linking of fullerene can be realized at the ends, on the sides, star-like, or between polymer chains. An interaction between functional groups of polymer and fullerenes based on donor-acceptor process can be realized too. Also an exfoliating nanocomposite arrangement of polymer and fullerenes is not excluded here. However the authors of the contribution are not able to precisely defined how is the fullerene C60 and C60oxi bound to the basic polymer of prepared nanofibers. Nevertheless the inhibitory effect of fullerene C60 or its derivative C60oxi was detected during the nanocomposite nanofibers thermo-oxidative degradation. This was probably due to interaction with the radicals generated by degradation of the polymer and the ability of fullerene to trap this reactive species. The scavenger effect of fullerene was also confirmed in the work [2] with the same fullerene derivative, in role of radioprotect

Table 2. Interpretation of the test results from PVB and PUR nanofibers measurements.

Nanofibers	Temperature of the decomposition beginning [°C]	$\Delta m/\Delta t$ [mg/min]	ΔH [kJ/kg]
1. PVB - C ₆₀ Oxi	337	0,15	-2374
2. PVB – blind sample	315	0,07	-2822
3. PUR – blind sample	237	0,17	2625
4. PUR - C ₆₀ (mixing in polymer solution)	275	0,15	3908
5. PUR - C ₆₀ (mixing in solvent at first)	288	0,14	-2641

$\Delta m/\Delta t$ – average rate of the sample weight loss

ΔH – thermal decomposition of color ($\Delta H < 0$ exothermic reaction, $\Delta H > 0$ endothermic reaction)

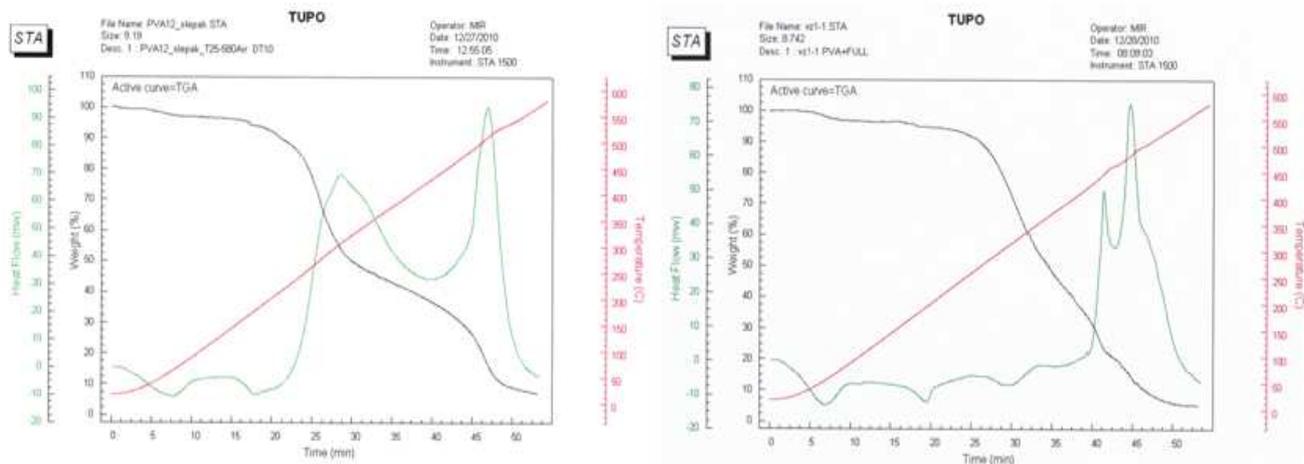


Fig 3. Thermal analysis graphs presenting blind sample of PUR nanofibers on the left side and PUR nanofibers with addition of C₆₀ (mixing in solvent at first).

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