JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 9, September 2009, p. 1319 - 1322

Polyoxyethylene assisted electrospinning of nanofibers from calcium phosphate sol solution♣

K. STARBOVA*, E. KRUMOV, D. KARASHANOVA, N. STARBOV
Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences
Acad.Georgi Bonchev Str., Bl.109, 1113 Sofia, Bulgaria

Non-woven mats comprised of calcium phosphate/polymer hybrid fibers with large aspect ratios and mean diameters in the nanosized range are synthesized, combining electrospinning and sol-gel techniques. High molecular weight polyoxyethylene and a sol from calcium and phosphorus organic precursors are used for preparation of the spinning solutions. The polymer/sol weight ratio, high tension and capillary tip to counter electrode (collector) distance are chosen as the processing parameters. A specially developed thermal procedure is applied in order to obtain polymer free fibers. Scanning electron imaging and wide angle X-ray diffraction are applied in order to follow the morphology and initial crystallization stages of the electrospun fibrous mats. Opportunities for designing a ceramic scaffold (network) built up of immobilized interconnected electrospun Ca-PO_4 fibers with mean diameters in the 100 – 250 nm range is demonstrated. Conclusions for the significance of the electrospinning as a simple, versatile and cost effective synthesis technique for the development of hydroxyapatite based materials are outlined.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: Hydroxyapatite fibres, Electrospinning, Sol-gel, Calcium phosphate

1. Introduction

Electrospinning could be regarded as a contemporary bottom-up approach for the synthesis of nanostructure fibrous materials with high aspect ratios and controllable grain sizes. Originally developed and subsequently proved on polymers [1], this technique has recently spread over a large number materials encompassing also refractory oxides [2,3] and other important ceramics like hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ [4,5]. Being a member of a large family of isomorphous substances, HA has a chemical composition that is similar to the inorganic, mineral part of human bones. For this reason, HA plays an important role in biological and structural aspects of the bone [6]. HA is a bioactive ceramic that is able to form, under a proper degree of crystallinity and porosity, a direct chemical bonding with the bone. The restoration of damaged human calcified tissue is promoted by particles or thin films on suitable implants [7]. The electrospun fibres are a relatively new material form of hydroxyapatite. The most successful experimental attempt for the synthesis of HA fibres down to a mean diameter of 200 nm refers to polyvinyl alcohol (PVA) assisted electrospinning of a calcium phosphorus sol [5]. The polymer molecular weight and viscosity of the spinning solution have been shown to determine the fibre mean diameter and porosity. A great variety of polymer/sol blend solutions have been experimented upon under single electrospinning conditions. Surprisingly, only one example of a scaffold-like fibre morphology has been demonstrated as evidence of the efficiency of the synthesis technique. Additionally, the post-processing of the as-spun mats does not envisage thermal conditions for preliminary PVA removal before the isothermal calcination, thus making reasonable the conclusion for the presence of carbon in the elemental composition of the fibres.

The present study represents a first step in the fabrication of calcium phosphate fibers via electrospinning using a high molecular weight linear polymer PEO (polyethylene oxide) and a calcium phosphate sol having a pH around the isoelectric point. POE was chosen as a partner, since it belongs to the family of low toxic and biocompatible polymers [8]. Also, PEO can be electrospun down to nanometer fiber diameters, and could assist the spinability of blend solutions [9,10]. We expect to combine the basic properties and advantages of the electrospun nanofiber mats and those of calcium phosphates, thus partially contributing to the increase in the wealth of engineered fibrous materials for biomedical and other specific applications.

♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

2. Experimental

The average M_v of PEO used was 800, 000.Calcium acetate monohydrate (CaAc) and tri ethyl phosphate (TEP), both Sigma Aldrich products of purity > 99% were used as calcium and phosphorus precursors for the preparation of the sol solution. The latter was made following the processing route for sol-gel synthesis of hydroxyapatite powders [11]. The CaAc was dissolved in distilled water. The TEP solution was added slowly drop wise, under magnetic stirring conditions, into the calcium-containing solution until the Ca:P atomic weight ratio reached a value of 1.67. The solution was aged for 24 hours. During that time period, the sol pH values change from 7.5 to 6.5, thus showing the occurrence of TEP hydrolysis.

The blend spinning solutions were prepared via mixing of 5 % or 3 % POE aqueous solutions and the Ca/PO_4 sol in the weight ratio 4:1. They were poured out in a plastic syringe with a metal capillary tip. The latter was connected to the electrode of a high-voltage power supply. A grounded copper collector, covered with an aluminium foil served as a counter electrode. The distance between the capillary tip and the counter electrode was varied in the range 15 - 28 cm. The applied field strength (AFS) between the capillary tip and counter electrode was kept constant at 1 kV/cm. A dense web of white hybrid fibers was collected on the aluminium foil. The as-spun hybrid fibers were subjected to a developed two stage thermal procedure at 120^{o}C and 360^{o}C, in the presence of low pressure oil free compressed air, providing conditions for the efficient removal of the emanating gases from the heated space and controlled PEO pyrolysis [9,12]. The fiber morphology and Ca/P ratio were studied with a Philips 515 scanning electron microscope (SEM) equipped with an EDX spectrometer. The initial crystallization stages of the thermally processed mats were verified by conventional wide angle X-ray diffraction (WAXRD). The specific electrical conductivity of the spinning solutions was measured on the basis of an original method developed in [13]. In order to determine the fiber diameter distribution, statistical measurements were performed using the computer software product Image J. A minimum of 20 fiber diameters were measured for each sample.

3. Results and disscusion

Two blend solutions and corresponding controls of 5 and 3 wt% aqueous solutions of POE were tested for fibre forming ability under the conditions of electrospinning described in Section 2. It was established that similarly to the pure polymer solutions, the mixed solutions are also capable of being electrospun in a fibre-like form. Accompanying X-ray elemental analysis showed the preservation of a Ca/P atomic ratio of 1.67 in both as-spun and thermally processed fibres.

Fig. 1 presents scanning electron micrographs of as-spun hybrid fibres obtained from a mixed solution with 5.0 wt% POE/Ca-P sol in a 4:1 weight ratio, at different capillary tip to counter electrode distances, and an AFS of 1 kV/cm. One can see the formation of defect free nanosized fibers. A comparison of mats of blend solution (a) and that of pure 5 wt% POE, electrospun under the same conditions, showed the occurrence of electrospraying in the latter case. Obviously, the viscoelastic properties of the solution and the process of jet drying during the time of flight to the collector are improved by addition of Ca-PO_4 sol to the polymer. An important prerequisite for fiber formation from the blend solution is the substantial increase of its specific electrical conductivity (8.85 mS/cm) as compared to that of pure 5 wt % POE solution (1.15 mS/cm). It is also seen from Fig.1 that an increase in the tip to collector distance (a-b) is accompanied by an approximately 25% decrease in the fiber mean diameter, which is evidence for a jet stretching efficiency increase. The histograms in Fig. 2 demonstrate this trend. The latter was observed on further increase of the tip to collector distance to 28 cm, at a reduced electrospinning rate.

Fig. 3 shows how the fibre morphology of the as-spun mats changes after POE removal by the thermal processing. It should be noted that the white colour of the thermally treated mats is always preserved, giving evidence for the efficiency of the latter. As seen from the scanning electron micrographs in Fig. 3, the fibre-like morphology in Fig. 1 is also preserved in this case. Obviously, the fibres contract predominantly in the radial direction during POE pyrolysis. Also, the removal of PEO from the fibres is accompanied by a sensitive decrease in their mean diameters by about 30%, as shown by the corresponding histograms in Fig. 4.

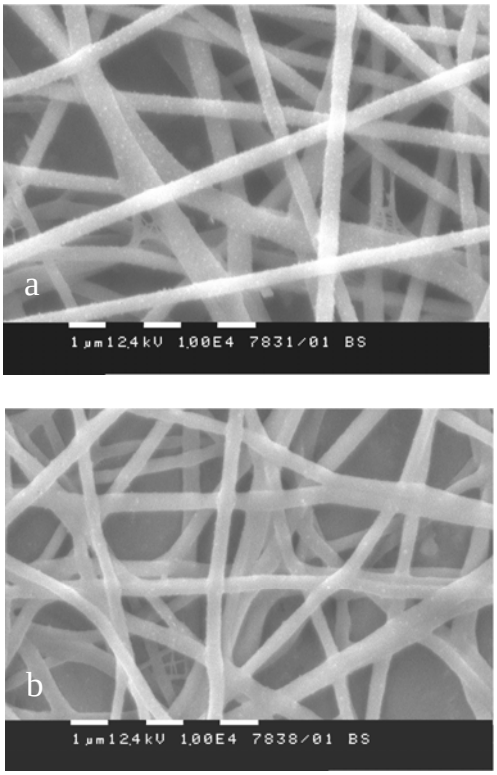

Fig. 1. Scanning electron micrograph of as-spun hybrid fibers;5,0 wt% POE/Ca-PO_4 Sol blend solution; AFS 1 kv/cm; tip to collector distance: 15 cm (a); 20 cm (b)

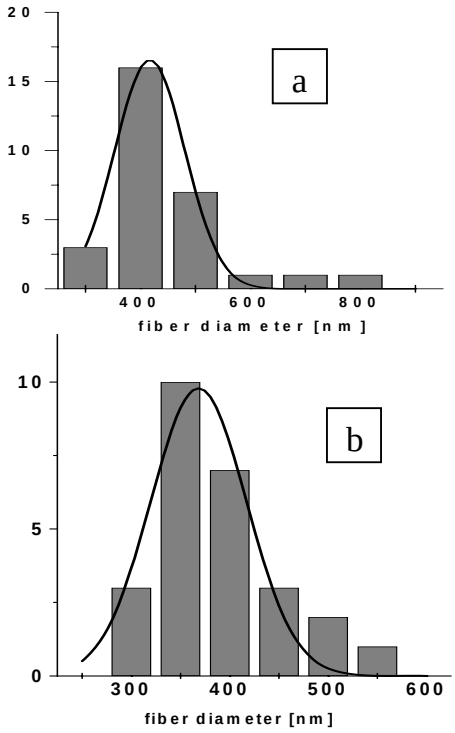

Fig. 2. Diameter distribution of as-spun hybrid fibers; 5,0 wt% POE/Ca-PO_4 blend solution; AFS 1 kV/cm; tip to collector distance:15 cm (a), 20 cm (b).

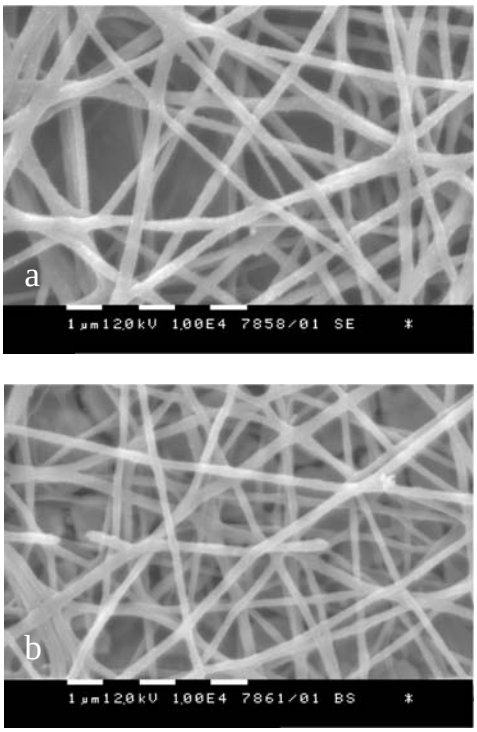

Fig. 3. As in Fig. 1, after POE removal via thermal processing.

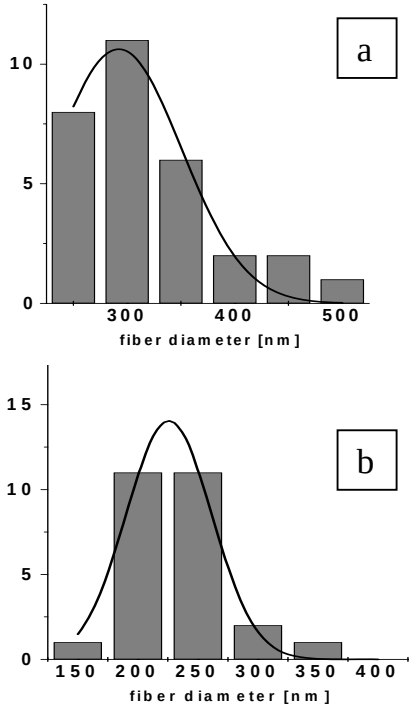

Fig. 4. As in Fig. 2, after POE removal

via thermal processing

The scanning electron micrographs in Fig. 5 show fibrous samples, electrospun from (a) 3 wt% PEO aqueous and (b,c) blend solutions (3 wt% POE/Ca-P sol, weight ratio 4:1). The formation of beads in the as-spun fibers of pure POE (a) and the defect free hybrid fibres as-spun (b) and after POE removal (c) is clearly seen. Also, the lower POE concentration and thermal processing result in an almost twofold decrease in the mean fiber diameters. Therefore, the capillary tip-to-counter electrode distance, as well as the polymer concentration, could be successfully used for governing the fiber mean diameter.

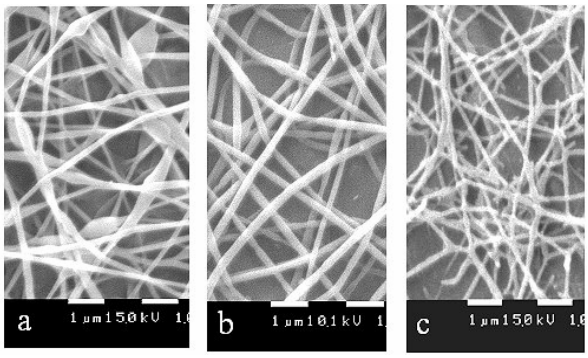

Fig. 5. Scanning electron micrographs of as-spun 3 wt% POE(a) and hybrid,(3 wt% POE/Ca-P) fibers,(b,c); AFS 1 kV/cm; tip to collector distance 20 cm (b);bar 1 µm

During the course of the experiments, XRD measurements were performed in order to check the state of the thermally treated POE free mats. The recorded WAXRD spectra display very low intensity peaks of hydroxyapatite and calcium carbonate, which is a first indication of the earliest crystallization stages occurring in the electrospun mats under the conditions of the thermal processing applied. The complete crystallyzation of the fibers via calcination of POE free fibers and preparation of crystalline hydroxyapatite fibers is complex problem that requires experimentation over a wide range of processing parameters, such as the heating rate, maximal temperature, environment, duration etc. These are objects of further experiments on real implant materials.

4. Conclusions

The results from the present study show how electrospun amorphous calcium phosphate fibers could be fabricated reproducibly and non-critically, with high aspect ratios, via POE assisted electrospinning. It is shown that some basic parameters of both the spinning solution and the electrospinning set up sensitively affect the mean fiber diameter. The opportunities for varying the ASF and polymer/sol solution weight ratios could further contribute to the reduction of the fiber mean diameter to below 100 nm.

Acknowledgements

The authors kindly acknowledge the Bulgarian Science Fund, Grant "NANOBIOMAT" under contract NT 4-02/2004. No.F-252 from the Ministry of Education and Science of Bulgaria.

References

[1] Formhals, US Patent **1,** 975, 504 (1934).
[2] D. H. Reneker, I. Chun, Nanotechnology, **7**, 216 (1996).
[3] G. Larsen, R. V.Ortiz, K. Minchow, A. Barrero, I. G. Loscertales, J. Am. Chem. Soc. **125**, 1154 (2003).
[4] Y. Wu, L. L. Hench, J. Du, K. L. Choy, J. K. Guo, J. Am.Ceram. Soc. **87,** 1988 (2004).
[5] X. Dai, S. Shivkumar, J. Am. Ceram. Soc. **90**, 1412 (2007).
[6] T. S. B. Narasaraju, D. E. Phebe, J. Mater. Sci. **31**, 1 (1996).
[7] U. Vijayalakshmi, S. Rajeswari, Trends Biomater. Artif. Organs **19**, 57 (2006).
[8] D. Herold,, K. Keil, D. Burns, Biochem. Pharmacol. **38**, 73 (1989).
[9] K. Starbova, E. Krumov, N. Starbov, M. Spasova, I. Rashkov, Nanoscience & Nanotechnology **6**, Eds. E. Balabanova, I. Dragieva, Heron Press, Sofia (2006), p.237.
[10] K. Starbova, M. Spasova, V. Yordanova, N. Starbov, I. Rashkov, J. Optoelectr. Adv. Mater. -Rapid Commun. **1**, 629 (2007).
[11] U. Vijayalakshmi, S. Rajeswari, Trends Biomater. Artif. Organs. **9**, 57 (2006).
[12] E. Neumann, H. Nadeau, Anal. Chem. **35**, 1454 (1963).
[13] N. Starbov, V. Denishev, D. Karashanova, NEWS Bulgarian Academy of Sciences. **1**, 1 (2008).

*Corresponding author: ilka@clf.bas.bg