CARBON NANOCOMPOSITE MEMBRANE WITH BIOACTIVE FILLERS

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Introduction

Carbon fibers are widely used in medical applications. All types of carbon materials (micrometric fibers, carbon nanotubes, graphene) show properties that are important for different kinds of implants. Some carbon materials may be applied on their own (CNT), while others are used to modify a polymer matrix (and used as composites, nanocomposites).

Electrospinning is a new technique to obtain fibers with a polymer characterized by submicrometric and nanometric diameter. The most important asset of such biomimetic fibers is their size and shape that imitate human tissues (ECM, collagen).

It seems purposeful to design a fibrous system conducive to bone regeneration. In the literature it is proved that carbon fibers obtained from polymer precursor (polyacrylonitrile, PAN) and then thermal treatment. Such fibers may be modified during a spinning process by adding bioactive nanoparticles (e.g. tricalcium phosphate, hydroxyapatite, bioglass or silica). Studies of similar - yet micrometric - compositions displayed their bioactive properties.

In the present work the electrospinning method was used to obtain nanocomposite fibers PAN/TCP and PAN/SiO_2 composed of nanometric and submicron fibers enriched with TCP or SiO_2 respectively. The fibers underwent two-stage thermal treatment: oxidation and carbonization. During these processes the structure of the base polymer changed. As a result, nanocomposite carbon fibers were produced (CNF/TCP and CNF/SiO_2). Morphological analysis of the fibers was conducted at every stage of the treatment. The properties of the final carbon substrate, including its bioactivity, were also assessed.

Materials and Methods

Commercially-available polyacrylonitrile (Sigma Aldrich) was used in the study (molecular weight 150 kDa, density 1.18 g/ml at 25°C). DMF (CZDA, Avantor) was used as a solvent. 12% polymer solutions were prepared and nano additives TCP and SiO_2 (5% wt) were dispersed in the solutions. Nanometric particles had the following sizes: SiO_2 5-10 nm (Sigma Aldrich), TCP 30-50 nm (Sigma Aldrich). The compositions were homogenized mechanically and then sonified before inserting them into the electrospinning machine. The fibers were obtained on the drum collector at 12 kV and 32°C. The oxidation process lasted for 30 minutes at 250°C. The carbonization took place in protective atmosphere (nitrogen) and it had two stages: 720°C/30min and 950°C/30min. The morphology of carbon fibrous membrane was established by means of SEM (Nova NanoSEM), while the presence of fillers (TCP, SiO_2) - using EDS analysis (Genesis). The diameters of nanocomposite fibers and their contraction after the thermal treatment were assessed, too. The nanocomposite membranes were incubated in simulated body fluid (SBF) for 7 and 14 days (37°C/5%CO_2) to run the bioactivity test. The SEM/EDS analysis confirmed bioactivity of the materials and the apatite growth on their surface. The structural tests were also conducted to establish the composition of the layer on the surface of the membranes (FTIR-ATR).

Results and Discussion

The polymer fibers with PAN measure approx. 350 nm in diameter. The addition of modifiers causes the diameter growth to 380 nm for TCP and 360 nm for SiO_2 respectively. Thermal treatment (oxidation) results in obtaining the fibers of 280 nm in diameter for PAN, 290 nm for PAN/TCP and 250 nm for PAN/SiO_2. In turn, carbonation influences the contraction growth of membranes: 150 nm (PAN), 180 nm (PAN/TCP) and 150 nm (PAN/SiO_2). EDS analysis indicates the presence of elements attributed to nanofillers: silicon for SiO_2, calcium and phosphorus for TCP (FIG. 1). However, the number of these elements is minimal. The PAN/SiO_2 membrane seems to be a more homogeneous composition. It is probably related to a smaller size of its particles (SiO_2: 5-10 nm). The incubation in SBF confirms the apatite growth on the CNF/TCP membrane after 7 days, whereas on the CNF/SiO_2 membrane it appears after 14 days. After that period of time on the CNF/TCP membrane no traces of fibrous substrate are visible. There is no apatite on the reference substrate of pure CNF.

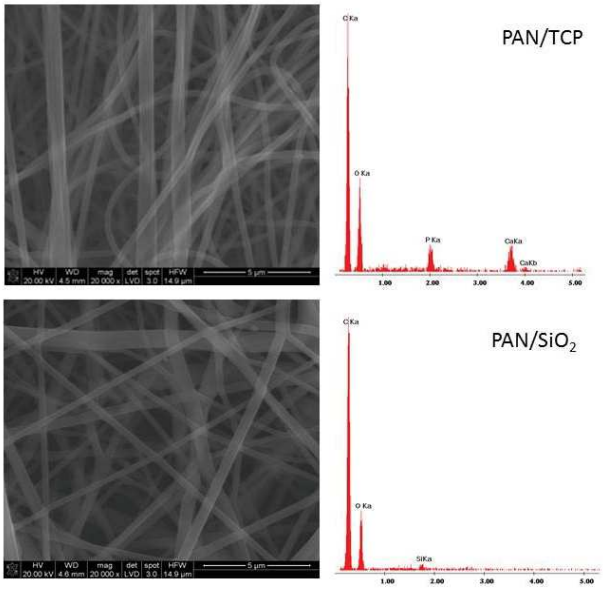

FIG. 1. Microstructure of polymer nanofiber (SEM/EDS) with PAN/TCP and PAN/SiO_2.

Conclusions

It was demonstrated that the electrospinning method makes it possible to obtain polymer nanocomposite membranes modified with TCP and SiO_2 respectively. Having undergone the thermal treatment, such fibers change into carbon fibers that are still nanocomposites: CNF/TCP and CNF/SiO_2. Both kinds of fibers display bioactivity in *in vitro* conditions (SBF).

Acknowledgments

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