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The structure and properties of the carbon non-wovens modified with bioactive nanoceramics for medical applications

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ABSTRACT

The paper presents the results of the manufacture of carbon fibers (CF) from polyacrylonitrile fiber precursor containing bioactive ceramic nanoparticles. In order to modify the precursor fibers two types of bio-glasses and wollastonite in the form of nanoparticles were used. The processing variables of the thermal conversion of polyacrylonitrile (PAN) precursor fibers into carbon fibers were determined using the FTIR method. The carbonization process of oxidized PAN fibers was carried out up to 1000 °C. The carbon fibers were characterized by a low ordered crystalline structure. The bioactivity tests of carbon fibers modified with a ceramic nanocomponent carried out in the artificial serum (SBF) revealed the apatite precipitation on the fibers' surfaces.

1. Introduction

Carbon fibers are at present used as a reinforcement for the production of advanced composite materials with polymer and metal matrices. It is due to the fact, that such composites display high specific strength and modulus and are corrosion resistant. Carbon fiber-reinforced polymers (CFRPs) can be more resistant and stiffer than conventional materials used for construction, and when the weight of the structure is a relevant feature, composites can become a very attractive solution [1]. Pure CF or in the form of CFRP has also attracted interest for applications in medicine due to their attractive mechanical and physical properties and confirmed good biocompatibility with the living organism. CFs were investigated in bone tissue regeneration, for the reconstruction of tendons and ligaments, cartilage losses, reconstruction of abdominal walls defects, as well as in the reconstruction of different parts of cervical section of trachea. It is also worth to mention, that CF-based composites have been widely used in biomedical equipment, e.g. as external stabilizers, bolds, and hip joint [2].

Three-dimensional fibrous scaffolds made of CF, due to their excellent mechanical and electric properties, represent an attractive biomaterial, particularly in bone and cartilage regeneration [3–5]. Furthermore, CF can be manufactured both in the micrometer and nanometer scales which make these materials attractive for the masses as a scaffold for tissue engineering [6,7]. Carbon fibrous scaffolds can be obtained by needling or electrospinning [8]. Non-wovens formed by these methods are characterized by an open pore system enabling tissue ingrowth and transport of nutrients and products of metabolism [9,10].

Although CFs are known to be biocompatible materials, they display disadvantage due to their bioinertness and poor bioactivity. These features of CF limit their wider use in medicine. For this reason attempts have been made to modify chemical properties of carbon fibers. Improvement of biological activity of carbon fibers can be achieved by filling a polymer precursor fibers with bioactive fillers including natural or synthetic HAp, bioglass or wollastonite [11,12].

The effect of incorporation of the bioactive glass into the PAN-based fibers was examined by Paluszkiewicz et al. [13]. The authors reported that bioglass causes the formation of apatite-like layer on the surface of composite nanofibers. In vitro studies exhibited better cell adhesion, proliferation, and osteogenic induction of bone marrow-derived mesenchymal stem cells cultured on the composite nanofibers, which suggested the higher bioactivity of composite nanofibers compared to pure PAN-based carbon nanofibers.

The modification of PAN precursor fibers with various fillers including carbon nanotubes and ceramic nanopowders has already been investigated in many papers [14–17]. Calcium phosphate-based coatings on carbon fibers were discussed [18].

The manufacture of CF from PAN precursor containing HAp or bioglass particles may create a promising biomaterial for structural implants. The combination of high mechanical properties of lightweight

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Table 1
Properties of the precursor fibers.

Sample	Degree of crystallinity [%]	Size of crystallites [nm]	Tenacity [cN/tex]	Elongation at break [%]
PAN	47	4.3	47.34 ± 1.80	11.51 ± 0.58
PAN_W	51	4.0	41.94 ± 1.25	14.33 ± 0.51
PB	51	4.3	48.58 ± 1.46	13.39 ± 0.55
PBH	55	4.6	40.90 ± 2.08	11.95 ± 0.88

carbon fibers with osteoproductive and osteoconductive properties of HAp and bioglass, makes them suitable for bone tissue regeneration [19,20].

The aim of this work was to manufacture carbon fibers from PAN precursor fibers containing bioactive ceramics. Processing variables for preliminary oxidation process and the carbonization were studied. The supramolecular structure and microstructure of the developed composite CF were also analyzed. Bioactivity of the modified CF was determined by immersion of the fiber samples in the simulated body fluid (SBF).

2. Experimental part

2.1. Materials

PAN precursor fibers modified with bioactive ceramics were manufactured by the wet spinning method from solution. The copolymer of trade name Mavilon Zoltek Company was used, having the following composition: 93–94 wt.% of acrylonitrile units; 5–6 wt.% of methyl acrylate and about 1% alkyl sulfonate. The copolymer was characterized by the intrinsic viscosity determined at 20 °C in DMF at 1.54 dl/g. For modifying PAN precursor fibers the following nanopowders were used:

- bioglass 45S5 from MO-SCJ HealthCare with the following composition: SiO_2-45%, Na_2O-24.5%, CaO-24.5%, P_2O_5-6%
- laboratory prepared bioglass by sol–gel technique at AGH Krakow (A2) having a molar composition: CaO-54%, SiO_2-40%, P_2O_5-6%
- laboratory prepared wollastonite ($CaSiO_3$) at AGH Krakow.

The powders were introduced at the stage of preparing the spinning solution in the amount of 3% by weight. Four types of fibers formed into non-woven samples were manufactured. The following symbols of non-woven samples were used in the work.

- PAN — PAN non-wovens without nanofiller (reference);
- PAN_W — non-wovens containing 3 wt.% wollastonite;
- PB — non-wovens containing 3 wt.% of bioglass A2;
- PBH — non-wovens containing 3 wt.% of 45S5 bioglass from O-SCJ HealthCare.

The detailed conditions for the manufacture of PAN fiber precursors are published elsewhere [21]. Properties of elementary fibers in non-wovens are summarized in Table 1.

The first step in manufacturing of non-wovens was the cutting of the fiber bundle to staple fibers of 45 mm length. Then, the fibers were subjected to carding process to obtain a fleece which is characterized by

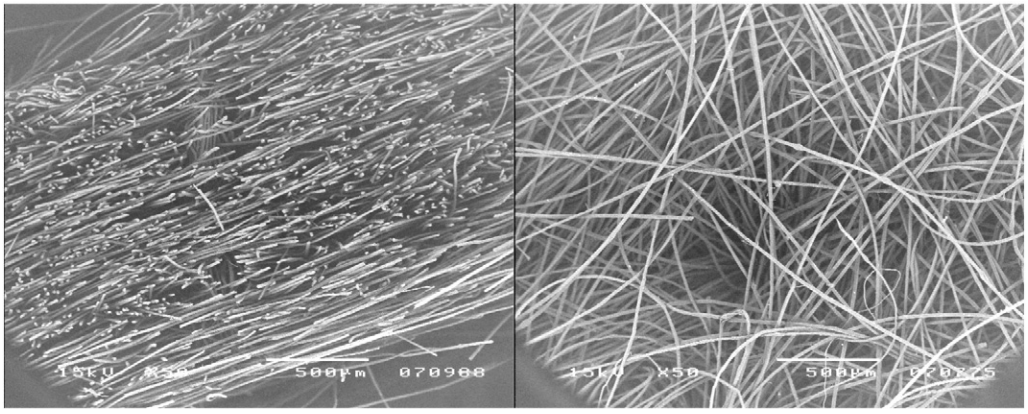

Fig. 1. SEM image of polyacrylonitrile non-woven without modifiers.

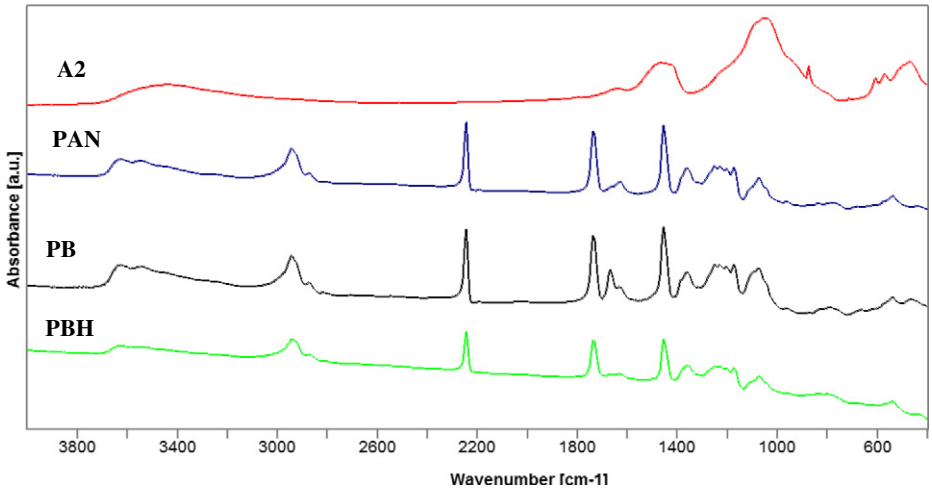

Fig. 2. FTIR spectra of AGH bioglass (A2), PB fibers containing AGH bioglass, PBH fibers containing 45S5 bioglass and unmodified PAN fibers.