EVALUATION OF PCL AND PCL/n-HAp FIBRES PROCESSED BY MELT SPINNING

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Abstract

In this work the process for the manufacture of polycaprolactone fibres containing hydroxyapatite nanoparticles by melt spinning method was developed. The effect of nanohydroxyapatite content on the fibre structure and properties was investigated with FTIR, SEM, DSC, TGA methods. The mechanical properties of obtained fibres enable further processing to scaffolds by nonwoven technologies.

Keywords: *PCL fibres, melt spinning, scaffolds, bone, tissue engineering*

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Introduction

Composite fibres comprising a biodegradable polymeric matrix with bioactive filers show considerable promise in the field of tissue engineering, potentially as nonwoven scaffold for bone regeneration.

Poly(ε-caprolactone) (PCL) is a biodegradable, semicrystalline aliphatic polyester which has been regarded as non-toxic and tissue compatible and was approved after extensive testing by the US Food and Drug Administration (FDA) to produce a number of medical and drug devices [1-2]. PCL can be transformed by melt spinning into fibers for subsequent fabrication of three dimensional scaffolds for bone tissue engineering applications. Unfortunately, PCL has an intrinsic hydrophobic chemical nature, and its poor interaction with biological fluids unables cells adhesion and proliferation [3-4]. Incorporation of synthetic nano-hydroxyapatite (n-HAp) into the fibrous polymer matrix can enhance biological properties (such as bioactivity) of the scaffold. Bioactive material in biological environment should be covered with apatite, similar to the natural one present in bones, which allows for bonding of biomaterial with bone. It is believed that the appearing of apatite on the implant surface (the process known as bioactivity) is leading to the formation of chemical bonds at the implant - bone interface [5-6]. It has been proven that the HAp, promotes osteoblast adhesion, differentiation and proliferation, osteointegration and deposition of calcium-containing minerals on its surface, which lead to enhanced formation of new bone tissue within a short period of time [7].

The aim of the present study is to develop a process for the manufacture of polycaprolactone fibres containing hydroxyapatite nanoparticles, as well as to assess the effect of hydroxyapatite content on the fibre structure and properties.

Materials and Methods

Fibre production

Polycaprolactone (Sigma-Aldrich) having a molecular weight of 70 000 - 90 000 g/mol was used in the study. Nano-hydroxyapatite was produced at the AGH-UST (Krakow, Poland). An average size of the n-HAp particles was 23 nm. PCL/n-HAp fibres were extruded from the melt using a prototype laboratory spinning machine PROMA (Torun, Poland). The applied forming equipment was a one-screw and one-headed extruder with an electric heating system. Its mass cylinder consist of two heating zones: supplying and mixing, respectively. The screw of the extruder has a characteristic roll shape crown of a cone enabling an effective process of mixing the components in the melt. Screw parameters are: diameter D_1=55 mm and D_2=21 mm, length L=245 mm. A polymer melt is pressed from the extruder to the spinning head equipped with a separate heating circuit, a passing-screw (D_p=55 mm, L=110 mm) and an exchangeable spinning die. Fibres were extruded from the melt with a temperature of 170°C and were spun with a take up velocity of 247 m/min. Nano-hydroxyapatite (5 w/w%) was added to the polymer powder before melting. The receiving of masterbatch of PCL/n-HAp, before the principal process of forming fibers was applied. The other parameters of the process of forming: rotation of the extruder screw and passer 9 and 10 rpm, respectively.

Methods

The surface morphology of the composite fibres was examined using scanning electron microscopy (SEM, Jeol JSM 5500). The average fibers' diameter was estimated from the SEM images. Chemical characteristics of the fibres were evaluated by FTIR method using spectrophotometer Nicolet 6700. The spectra were recorded at the range of 400-4000 cm^{-1} using at least 64 scans and 4 cm^{-1} resolution. The mechanical properties of electrospun samples were measured by uniaxial testing machine (Zwick-Roell Z 2.5.). All tensile tests were done on single fibre samples. The individual fibres were mounted on paper tabs, with a central cut-out that gave a gauge length of about 25 mm. The tab was gripped in the jaws of the testing machine and, prior to testing, cuts were made from each side to the central cut-out.

Thermal properties of studied fibres were estimated by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) methods. Calorimetric investigations were carried out on a TA Instruments Thermal Analysis System 5100 equipped with a MDSC Calorimeter 2920 at following conditions: heating rate 10°C/min, nitrogen gas flow (40 ml/min), temperature up to 300°C. Thermogravimetric measurements were done using TA Instruments Q 500 TGA Analyzer up to 800°C at the other conditions mentioned above. The thermograms were evaluated by means of the Universal V2.6D (TA Instruments) software.

Results and Discussion

The microstructures of the pure PCL and n-HAp modified PCL fibres (PCL/n-HAp), produced by melt spinning process, are presented in FIG. 1. Hydroxyapatite agglomerates are clearly visible on the surface of the PCL/n-HAp fibres (FIG. 1b). The distribution of fibres diameter is shown in FIG. 1c. Polycaprolactone fibre diameter is in the range of 28-53 μm, while the calculated average diameter for the PCL fibres is 35.6 ±10 μm. In the case of composite fibers, the PCL/n-HAp fiber diameter is in the range of 19-53 μm and average diameter is slightly smaller (31.4 ±7 μm). FTIR spectra recorded for PCL, PCL/n-HAp and n-HAp samples are presented in FIG. 1d.

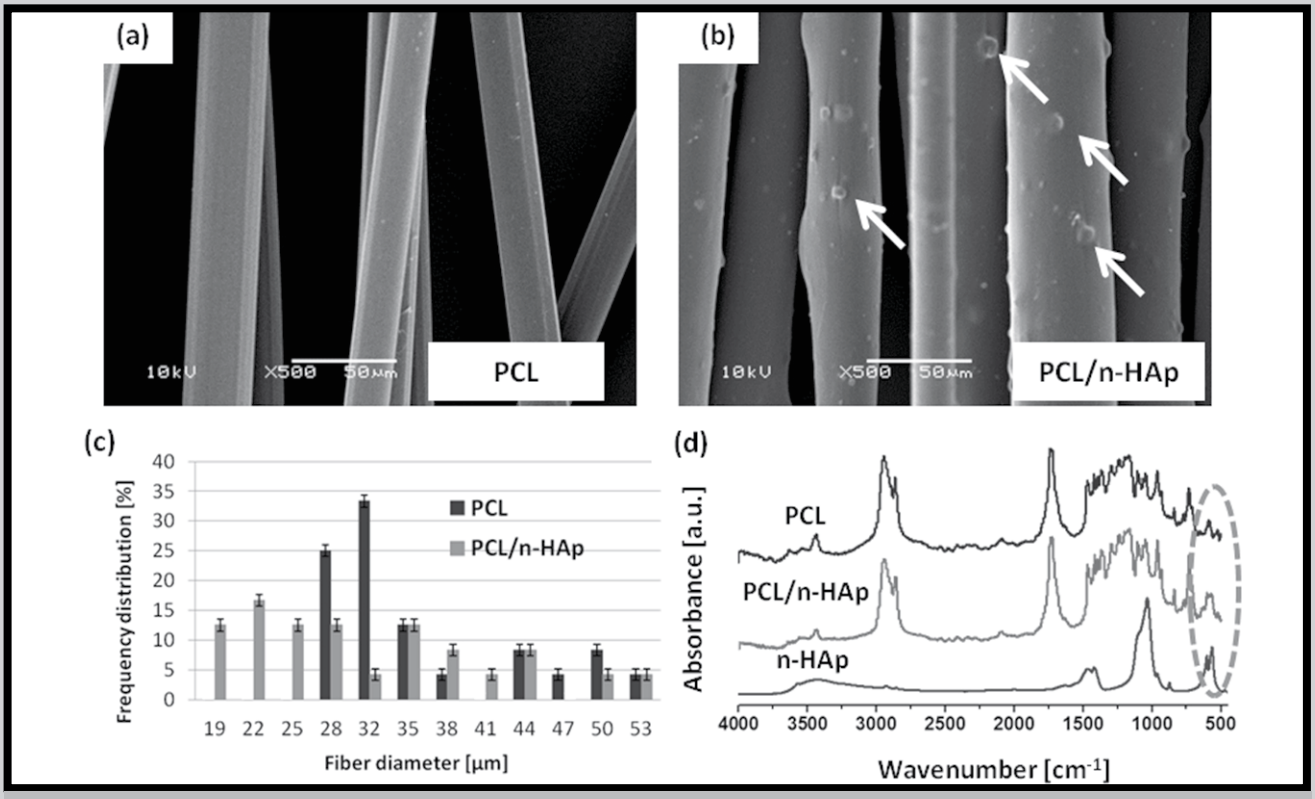

FIG. 1. Microstructure of (a) polycaprolactone fibres (PCL); (b) polycaprolactone fibres modified with hydroxyapatite (PCL/n-HAp); (c) Fiber diameter distribution for PCL and PCL/n-HAp fibers; (d) The comparison of FTIR spectra of PCL, PCL/n-HAp and n-HAp samples.

The most important characteristic bands for polycaprolactone are shown in TABLE 1. FTIR analysis confirmed apatite presence in the PCL matrix. Typical force-elongation curves for the PCL and PCL/n-HAp fibers are presented in FIG. 2a,b. The highest value of tensile force (0.24 N) was observed in the case of pure PCL fibres whereas the largest elongation (about 220 mm) was observed in the case of composite fibres (PCL/n-HAp). Tensile strength for both samples is similar (FIG. 2c). The mechanical properties of obtained fibres enable further processing to scaffolds by nonwoven technologies. DSC investigations revealed the quite good thermal stability of PCL melt irrespective of modification with n-HAp up to 300°C and the distinct decrease of the melting enthalpy value in the case of fibres with n-HAp in respect to PCL fibres without the modifier (FIG. 3). The results of TGA measurements showed one-stage thermal decomposition of PCL and PCL/n-HAp fibres with the maximum at 401°C (FIG. 4).

TABLE 1. Assignment of FTIR bands for polycaprolactone.

Wavenumber [cm^{-1}]	Type of vibration
2949	CH_2, asymmetric, stretching
2865	CH_2, asymmetric, stretching
1727	C=O, stretching
1293	C-O, C-C, stretching
1240	C-O-C, asymmetric, stretching
1175	C-O-C, symmetric, stretching
1157	C-O, C-C, stretching

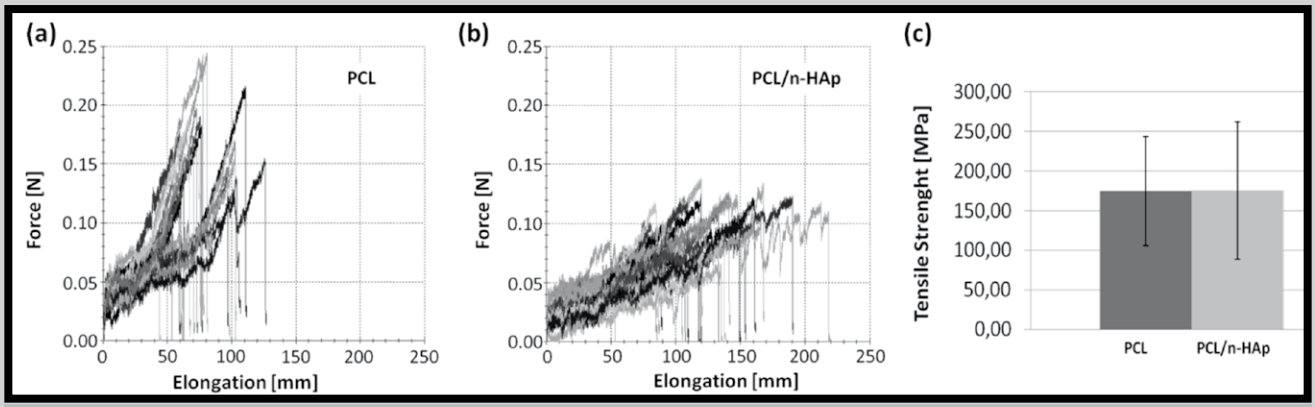

FIG. 2. (a-b) Force-elongation curves obtained from tensile tests performed on melt spun PCL and PCL/n-HAp fibers; (c) Tensile strength of melt spun fibers.

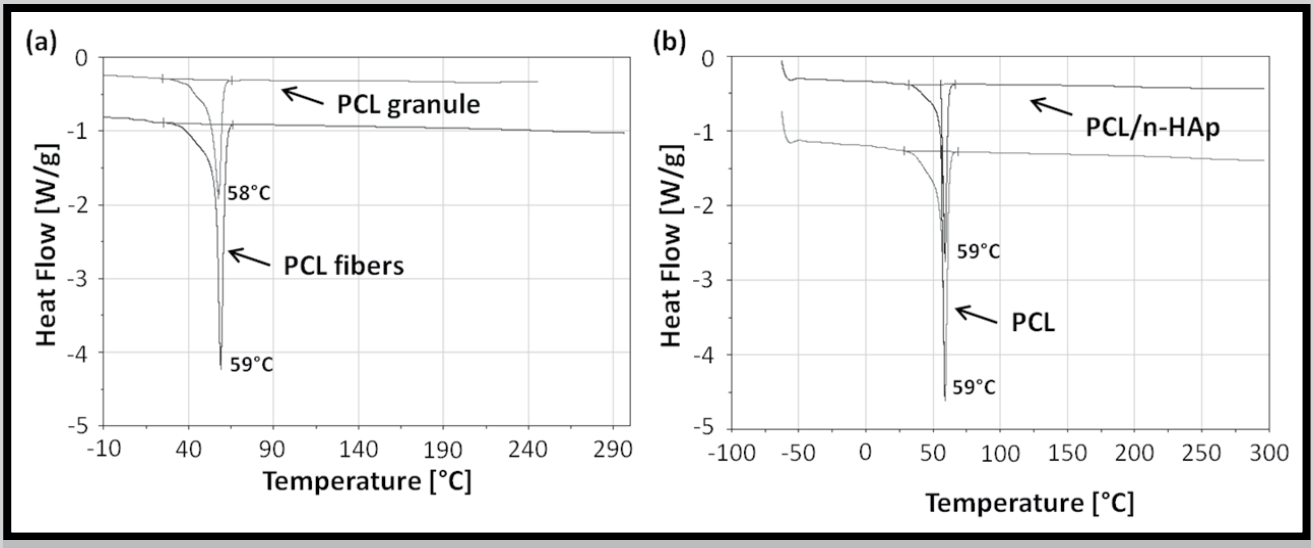

FIG. 3. DSC thermograms of (a) PCL granule and PCL fibers; (b) PCL and PCL/n-HAp fibers.

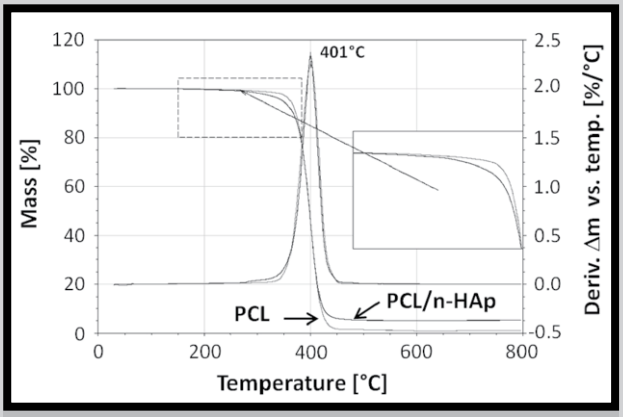

FIG. 4. TGA curves of melt spun PCL and PCL/n-HAp fibers.

Conclusion

The results obtained in this paper indicated that incorporation of the n-HAp particles in the polymer matrix during melt spinning process induced interesting changes in the material surface morphology. SEM observations and FTIR analysis may possibly suggest the presence of an apatite on the surface of fibres. The mechanical properties of obtained fibres enable further processing to scaffolds by nonwoven technologies. Our preliminary study suggests that the PCL/n-HAp fibres may be potentially useful in tissue engineering applications, particularly as three dimensional substrates for bone growth.

Acknowledgments

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