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Biodegradation of bicomponent PCL/gelatin and PCL/collagen nanofibers electrospun from alternative solvent system

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ABSTRACT

Bicomponent polycaprolactone/gelatin and polycaprolactone/collagen nanofibers formed by electrospinning using various solvents were subjected to biodegradation and compared. Hexafluoroisopropanol (HFIP) was used as a reference solvent, while the second, alternative solvent system was the mixture of acetic acid (AA) with formic acid (FA). Biodegradation of investigated materials was manifested mainly by the gelatin leaching, including collagen which is indeed denaturated to gelatin during electrospinning, leading to nanofibers erosion. There was no molecular degradation of PCL during 90 days of biodegradation procedure as deduced from no change in the elongation stress at break. The rate of biopolymer leaching was very fast from all materials during the first 24 h of biodegradation, being related to surface leaching, followed by a slower rate leaching from deeper material layers. Mass measurements showed much faster biopolymer leaching from nanofibers electrospun from AA/FA than from HFIP because of strongly emulsive nature of the solution in the former case. Irrespective of the solvent used, the leaching rate increased with initial content of gelatin. The analysis of Young modulus during biodegradation indicated complex mechanism of changes, including biopolymer mass loss, increase of PCL crystallinity and partial gelatin renaturation.

1. Introduction

It is a fact that tissue engineering is dynamically evolving research area, whether we think of cellular stimulation methods, novel multifunctional materials or cutting edge technologies. The trend toward biomimetism has been observed for years, making electrospinning, though not a new idea itself, a technique that has still a lot of to offer, considering a remarkable structural similarity of electrospun materials to extracellular matrix.

Materials made of polycaprolactone have been present in scientific literature focusing on scaffolds for tissue engineering for a couple of years now [1–4]. Polycaprolactone belongs to a group of biodegradable aliphatic polyesters, has good mechanical properties and is not cytotoxic. In comparison to other materials from this group it has lower mechanical stiffness and its degradation products do not cause a decrease in pH in an area surrounding a graft, what has been reported for polylactide or polyglicolide and may increase inflammation [5,6].

As any other aliphatic polyester, polycaprolactone is hydrophobic, what is the disadvantage for materials used in scaffolds. This problem can be solved by an addition of highly hydrophilic substance. Gelatin is a biopolymer derived from collagen, the major extracellular matrix building protein. Incorporating gelatin or collagen into polycaprolactone scaffold, not only allows to decrease significantly hydrophobicity, but also has a favourable influence on cellular response of a material. Electrospun nonwovens from PCL/gelatin and PCL/collagen structurally mimic native extracellular matrix and also provide cells with chemical cues affecting them. Collagen and gelatin contains Arg-Gly-Asp (RGD) amino acid sequences that can be found in many naturally occurring proteins. Integrins (cell binding proteins) recognize those sequences and promote cell adhesion [7]. This way biopolymer addition increases cell attachment and spreading to the surface of a material. Furthermore, nanofiber materials from PCL/biopolymer exhibit better mechanical properties than the ones made of any of them individually.

Electrospinning of bicomponent nanofibers requires the use of a solvent which dissolves both of the polymers. To date, the most common compounds used in such systems were perfluorinated

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Table 1
Abbreviated names of all investigated materials.

PCL content [% w/w]	Biopolymer content [% w/w]		Abbreviation	
			A – AA/FA	H – HFIP
100	0		PA	PH
90	G – gelatin	10	PGA 9:1	PGH 9:1
80		20	PGA 8:2	PGH 8:2
70		30	PGA 7:3	PGH 7:3
90	C – collagen	10	PCA 9:1	PCH 9:1

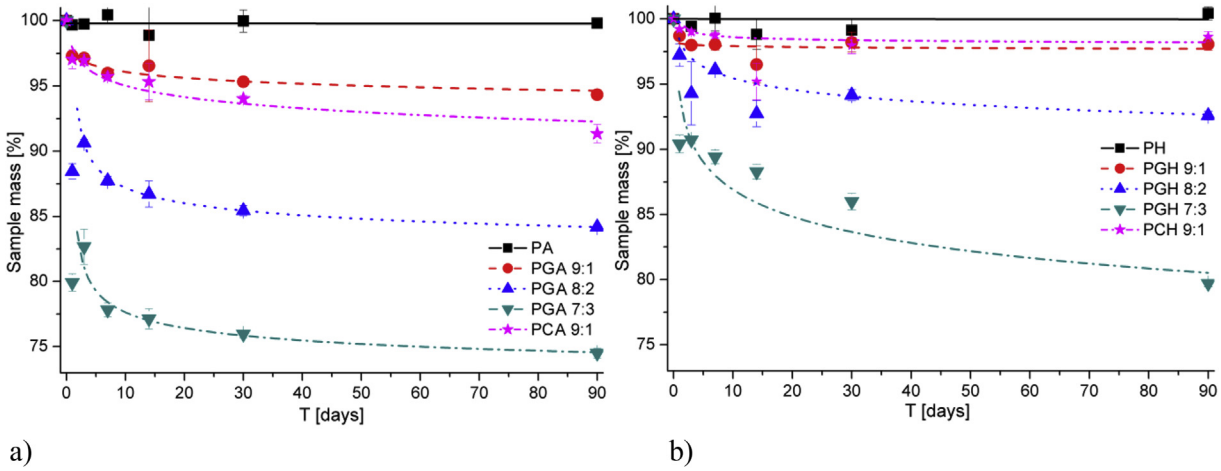

Fig. 1. Sample mass loss after biodegradation normalized to the total sample mass a) AA/FA and b) HFIP.

alcohols such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and 2,2,2-trifluoroethanol (TFE). These solvents are expensive and classified as highly toxic. We have optimized the process of electrospinning of PCL/gelatin and PCL/collagen nanofibers based on the use of alternative, relatively non-toxic solvents system composed of 90% of acetic acid and 10% of formic acid [8].

The application of the mixture of these acids reduces costs and toxicity of electrospinning. The disadvantage of this solvent system is the fact that polymer solution becomes emulsive, which is not observed in solutions from perfluorinated alcohols.

The aim of this work was to investigate whether the solvent used in electrospinning influences the kinetics of biopolymer leaching from bicomponent nanofibers and how the properties of electrospun material are affected by this process.

2. Materials and methods

2.1. Materials

PCL (Mn = 80,000 g/mol) and gelatin from porcine skin Type A (gel strength ~ 300 g Bloom) were purchased from Sigma-Aldrich Co., as well as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and phosphate buffered saline tablets (pH 7,4). Collagen Type I lyophilized from calf skin was purchased from Elastin Products Company, Inc.

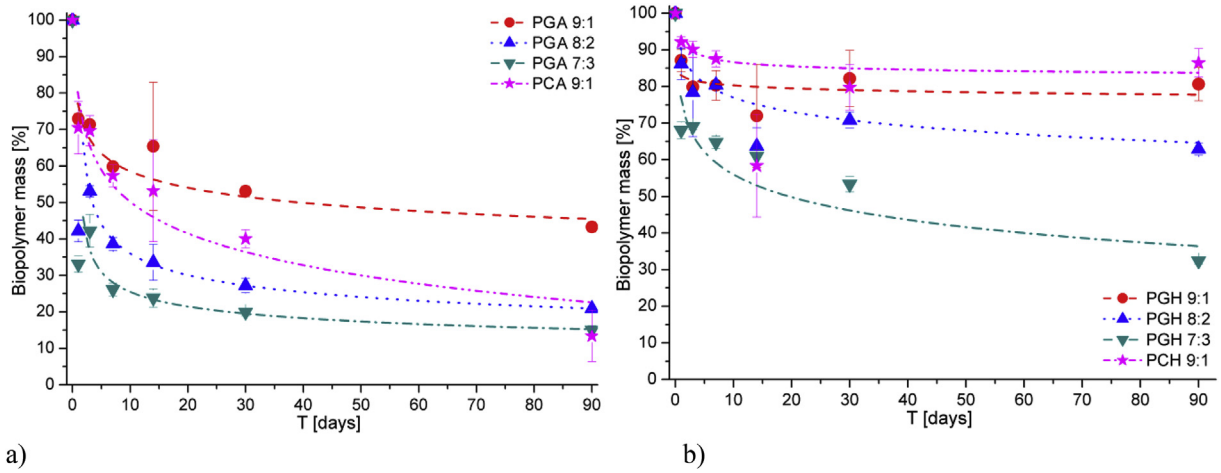

Fig. 2. Sample mass loss after biodegradation normalized to the biopolymer mass (biopolymer mass loss) a) AA/FA and b) HFIP.