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The Influence of Short-Term Simulated Body Fluid Storage on the Mechanical Properties of Composites Based on Polyamide Fibers and PDMS matrix modified by CaP nano/micro particles

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Abstract: Fabric composite materials for use as bone filling elements and bone substitutes have been investigated. The composites were composed of polyamide fibers and a matrix based on polydimethylsiloxane (PDMS). In order to increase the bioactivity, the matrix was modified by calcium phosphates (CaP) nano/micro particles, namely hydroxyapatite (HA), and β-tri-calcium phosphate (β-TCP) particles were used. A study was made of the effect of short-term storage (up to 56 days) in simulated body fluid (SBF) on the elution of the composite materials. Subsequently, their mechanical properties were tested. The changes in their material properties after being stored in the medium are discussed.

Keywords: Composite, CaP, PDMS, Polyamide, SBF

1. Introduction

Numerous synthetic bone graft replacement materials are nowadays available. These single-phase and multi-phase (i.e., composite) materials combine the advantages exhibited by each component of the material, with a structure and composition similar to that of the natural bone [1]. Bone as a natural composite comprises two main components, i.e. organic and inorganic materials. The organic portion of the bone comprises cells as well as the fibrous and amorphous part of the extracellular matrix. The fibrous part is formed by collagen fibers, and the amorphous part is

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formed by various glycoproteins or glycosaminoglycans that play important roles in controlling the function of osteoblasts as well as bone tissue mineralization [1, 2]. The inorganic component comprises minerals, particularly HA and calcium phosphates. Another important feature of natural bone tissue is its nanoarchitecture. It has been observed that nanocrystalline HA promotes the adhesion, proliferation and differentiation of osteoblasts. Moreover, the deposition of calcium-containing minerals on nanocrystalline HA was higher than on microcrystalline HA [3]. The mechanical properties of the natural bone should also be taken into account when designing an artificial bone implant. Suitable mechanical properties of the artificial material, similar to those of the natural bone, can induce the differentiation of stem cells toward osteoblasts when this cell type is lacking [4].

Composite materials based on polyamide fabrics, PDMS matrix and four kinds of CaP additives were used in this study. Polyamide fabrics were used because of their mechanical stability and biocompatibility. Polyamide monofilaments were used for constructing a non-resorbable, long-lasting and stress-absorbent reinforcement for designing articular disc substitutes [5]. In Springer's study, polyamide also promoted the adhesion of human or porcine fibrocartilage cells in cultures derived from the temporomandibular joint, and showed no toxicity to these cells. In addition, poly(hexamethylene adipamide), i.e., a polyamide containing carboxyl and amide groups similar to collagen, was successfully used for preparing a biomimetic composite with nano-hydroxyapatite, matching well the mechanical properties of the natural bone [6].

Although siloxane materials are hydrophobic, they generally allowed the adhesion, growth and differentiation of osteoblasts. Their osteoinductive behavior was further enhanced when they were rendered hydrophilic by exposure to an oxygen plasma treatment or by microtexturing their surface [7, 8]. Composites based on polymethylphenyl siloxane resins (produced by Lučební závody, Kolín, Czech Republic) promoted their colonization with human osteoblasts of the line hFOB 1.19 [9]. Another siloxane, i.e. 3-(glycidoxypropyl) trimethoxysiloxane, was used for constructing a bioactive composite with gelatin and Ca^{2+} ions, which stimulated the proliferation and differentiation of mouse osteogenic MC3T3-E1 in vitro. When these reinforcements were soaked in a simulated body fluid, apatite was formed by the reaction of a hydrated silica gel surface (Si-OH groups) and Ca^{2+} ions [10].

HA and TCP additives were chosen because they can mimic the crystalline mineral component of the bone. Inclusion of HA nanofibers in a beta-tricalcium phosphate (β-TCP) matrix significantly improved the mechanical properties of this material, especially its strength and toughness [11]. HA-containing materials act as sources of calcium ions, which are known to stimulate osteoblast proliferation and differentiation [10]. In addition, hydroxyapatite crystals can serve for nanopatterning the pore walls in order to enhance the osteoinductive activity of our newly constructed materials, as mentioned above [12, 13]. However, HA by itself has an inadequate mechanical property - especially low mechanical strength and increased brittleness. It is mainly applied in the form of bone fillers of various shapes for unloaded implants and in the form of a coating material on metallic prostheses, in

dental or maxillofacial applications [1]. Application of HA as composite matrix additives should overcome these problems. The interaction rate between the body and the artificial particles depends on their microstructure, morphology and size (e.g. nano/micro size).

The degradation behavior of polymeric composites on exposure to environmental conditions is one of the most important issues when dealing with them. Moisture absorption, especially in parts subjected to an aggressive environment or sterilization through heat, including water vapor treatment, leads to reduced mechanical properties and a change in dimensions. It is important to study the moisture absorption behavior in order to estimate the influence on the mechanical and structural properties of the composites. The aim of this study was to investigate the moisture absorption behavior of PDMS/polyamide/CaP hybrid composites during short-term immersion in simulated body fluid (SBF), which simulates the inorganic part of human blood plasma, at 37 °C for up to 56 days.

2. Materials and Methods

A composite material based on fabric reinforcement (aramid balanced fabric, based on aromatic polyamide fibers HM 215, Hexcel, FR) and a polysiloxane matrix M130 (Lučební závody Kolín, CR) was prepared, when HA and/or β-TCP powder (Berkeley Advanced Biomaterials Inc., San Leandro, CA, USA), average particle size 100±50 nm and/or 100±50 μm, was inserted into the matrix in amounts of 0, 5, 10, 15 vol.% (powder/matrix). Impregnated layers were placed into the curing mould (with the same orientation of the warp and the weft [0°/90°]) and finally cured under pressure 1.1 MPa at 225 °C in an air atmosphere for 4.5 hours and postcured under pressure 1.1 MPa at 250 °C for 4 hours. The specimens were immersed in SBF (ISO 23317) at 37 °C for 0, 14, 28 and 56 days under static conditions. After soaking, the modulus of elasticity in bending and the ultimate strength in bending in the direction of the fiber axis were determined by a four-point and/or a three-point bending set-up with the Inspekt 100 HT material tester (Hagewald & Peschke, Germany), in accordance with ISO 14125. Additionally, the open porosity of all composite samples before and after soaking in SBF was measured according to ASTM C-373. The sample nomenclature (differing by additives applied) is as follows: n-HA (nano HA), n-TCP (nano TCP), m-HA (micro HA) and m-TCP (micro TCP). Six samples from each group with dimensions of 60x7x2 mm (length x width x thickness) were applied. A statistical analysis for all tests was carried out by nonparametric analysis of variance, at a significance level of 0.05 (Kruskal-Wallis test, Mann-Whitney as a post hoc test), and the confidence intervals for the mean values were calculated at a significance level of 0.05.

3. Results and Discussion

The modulus of elasticity in bending and ultimate strength in bending / HA (TCP) volume fraction relationships after soaking periods were determined (see Fig. 1, 2). The open porosity of the composites before and after soaking in SBF is listed in Table 1.

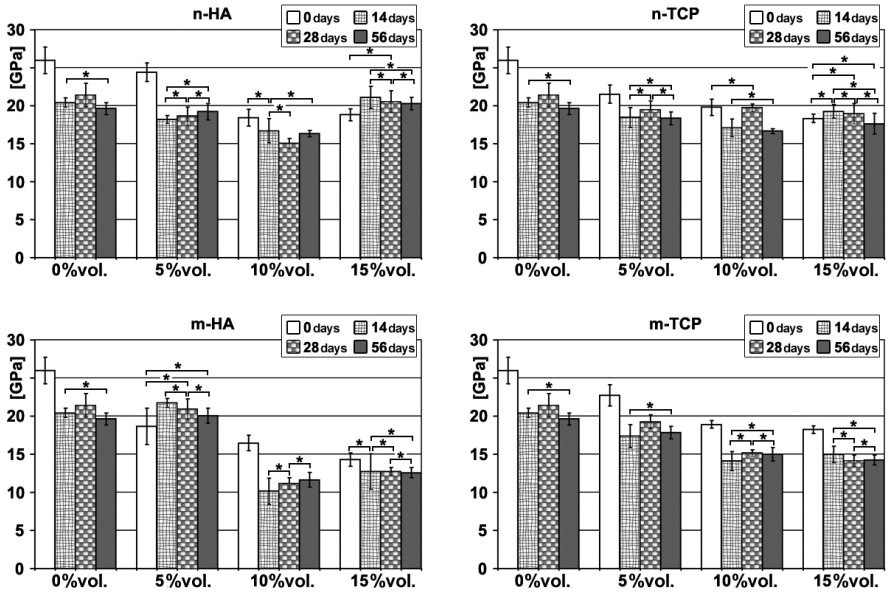

Fig. 1. Modulus of elasticity in bending of the composites before and after soaking in SBF (* denotes values without statistically significant differences)

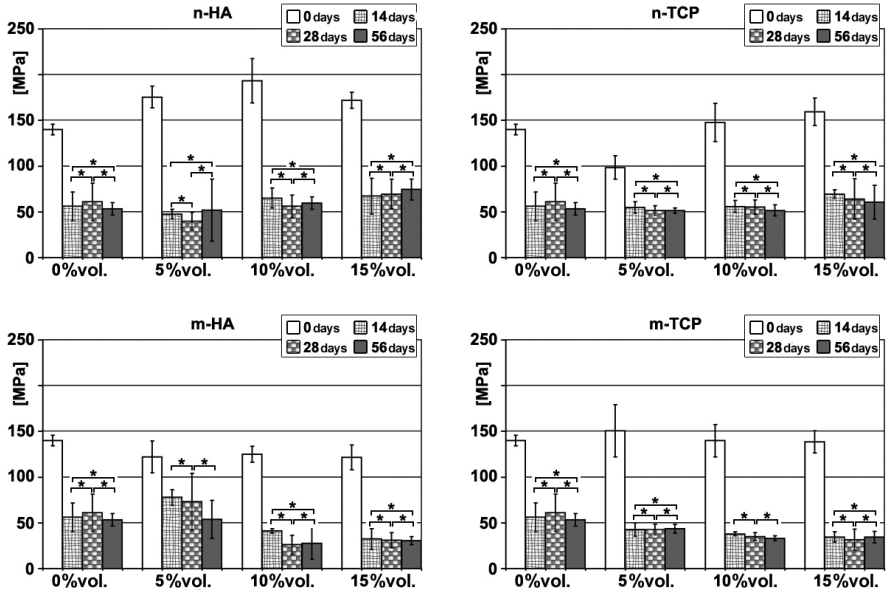

Fig. 2. The ultimate strength in bending of the composites before and after soaking in SBF (* denotes values without statistically significant differences)

Table 1. Open porosity of the composites before and after soaking in SBF (with confidence intervals at a significance level of 0.05)

		0 days		14 days		28 days		56 days	
		por.[%]	+/–	**por.[%]**	+/–	**por.[%]**	+/–	**por.[%]**	+/–
	0%	**20.19**	1.60	**16.91**	1.60	**20.68**	0.94	**20.11**	1.52
n-HA	5%	**15.39**	2.70	**17.44**	1.08	**15.25**	0.45	**16.28**	1.16
	10%	**15.78**	0.80	**19.12**	2.76	**14.04**	0.78	**13.97**	1.00
	15%	**13.96**	0.44	**14.07**	0.48	**13.43**	0.45	**14.23**	1.93
n-TCP	5%	**15.48**	0.19	**16.53**	0.57	**16.27**	0.97	**16.44**	1.99
	10%	**11.71**	3.24	**15.42**	1.18	**14.69**	0.54	**14.79**	0.21
	15%	**14.22**	0.37	**13.28**	0.03	**12.79**	0.72	**13.59**	0.58
m-HA	5%	**16.57**	0.51	**17.90**	0.59	**19.74**	2.20	**19.53**	2.88
	10%	**16.02**	1.67	**18.16**	2.65	**18.57**	0.83	**17.04**	0.39
	15%	**17.86**	0.27	**20.50**	2.50	**18.35**	0.35	**18.42**	0.56
m-TCP	5%	**16.73**	0.87	**17.12**	0.13	**16.96**	0.76	**16.21**	0.16
	10%	**18.68**	2.19	**16.76**	1.18	**16.95**	0.42	**15.48**	1.17
	15%	**18.23**	0.74	**18.15**	0.53	**19.92**	3.90	**15.99**	0.29

The modulus of elasticity in bending has been shown in all cases to be a function of exposure to SBF. In the case of both modified and unmodified composites, all values decrease after 14 days of soaking in SBF. This is a decrease in general of 20% in comparison with samples unexposed to SBF. In the case of ultimate strength in bending, the strength was shown in all cases to be a strong function of exposure to SBF. In values measured after a 14-day period there is in general a decrease of 50-60% in comparison with samples not exposed to SBF. After 28 and 56 days, the two mechanical property values remain equal, without statistically significant differences. Despite the decreases shown above, the modulus and strength values both remain in the range quoted for cortical bone.

Statistically significant differences can be found in the comparison between the composites modified by micro and nano additives. The composites modified by micro additives show a greater decrease in both modulus and strength in comparison with the values for the composites modified by nano additives. The changes in matrix-reinforcement interface adhesion can be deduced from the 20% decrease in the case of modulus of elasticity in bending and above all from the 50-60% decrease in flexural strength. The flexure strength, affected mainly by this adhesion, shows a greater decrease than in the case of the modulus, which is particularly affected only by adhesion. A possible explanation for this effect may be the influence of micro particles on increasing open porosity (see Table 1). The open porosity of the composites modified by micro additives, especially by 15 %vol., is statistically significantly higher than the porosity of the composites modified by nano additives. From this fact, and also from the decrease in the mechanical properties of the unmodified composites, we can deduce that the amount of additives influences the mechanical properties during exposure to SBF, above all due to its influence on increasing the open porosity. Erosion of the physico-chemical bonds between particular composite elements can occur at a higher rate in composites with higher open porosity values. A further explanation may lie in the absorptivity of the individual composite elements. An important finding for interpreting this decrease is

that there is a similar course in the changes in the mechanical properties in the case of an unmodified composite. The moisture absorption of aramid fibers is probably another factor that influences the process. The influence of the chemical composition of the additives on changes in the mechanical properties could not be demonstrated on the basis of the statistical analysis that was carried out.

4. Conclusions

A study has been made of the effect of a simulated body environment on mechanical properties by short-term storage of composites in SBF. The aim of the study was to assess potential changes in mechanical properties during exposure to SBF, and to verify to what degree modifications (5, 10, 15 %vol., nano/micro, HA/TCP) can influence the mechanical properties of the composites after the maximum soaking period. The chemical composition of the applied additives has no statistically significant influence on changes in the mechanical properties during exposure to SBF. Unlike the chemical composition, the particle size of the additives generally does have a statistically significant influence on mechanical properties. This influence is possibly due to changes in open porosity (higher values in the case of micro additives). The application of nano additives has a more favourable effect on the stability of the mechanical properties during exposure to SBF.

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