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BIOCOMPATIBILITY OPTIMIZATION OF FABRIC COMPOSITES BY CALCIUM PHOSPHATES

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Abstract: Composite materials based on a polyamide fabric and a polysiloxane matrix were designed for application in bone surgery. In order to increase the bioactivity, 2, 5, 10, 15, 20 and 25 vol. % of nano/micro hydroxyapatite (HA) and tricalcium phosphate (TCP) particles were added. The effect of the additives on the mechanical properties was studied and changes in the inner structure of the composites were investigated by means of image analysis. It appears that in comparison with the micro particles, the nano additives have a more favourable effect on mechanical properties. From the point of view of the final application of the composites as substitutes for hard tissues, 10 – 15 vol. % of nano additives is an optimum amount: in this case both the optimization of the toughness and the increase in the ultimate strength in bending occur without any changes in the inner structure of the composite.

1. Introduction

A successful product of tissue engineering must necessarily result from combining several disciplines dealing with mechanical properties, the interaction of the implant with the surrounding tissue, and also practical clinical experience. With composites consisting of polymer reinforcement and a polymer matrix with the possibility of selecting the volume ratio of the fiber reinforcement to the matrix and also a suitable orientation, mechanical properties identical with those of human bone can be obtained [1]. The reason for their wide use in various medical applications is mainly the availability of materials with various properties in various forms and compositions as well as the fact that they can be hardened directly into the required shape or structure with the most suitable fiber orientation, e.g., with respect to the direction of the acting load. Their biocompatibility and mechanical properties can also be enhanced by inserting a bioactive component into the matrix [1].

Polyamide fabrics were chosen because of their mechanical stability and bioactivity. Polyamide monofilaments were used for constructing a non-resorbable, long-lasting and stress-absorbent reinforcement for designing articular disc substitutes [2]. 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

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hydrophilic by exposure to an oxygen plasma treatment or by microtexturing their surface [3]. Composites based on polymethylphenyl siloxane resins (produced by Lučební závody, Kolín, CR) promoted their colonization with human osteoblasts of the line hFOB 1.19 [4]. 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 [5]. 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 [6]. HA-containing materials act as sources of calcium ions, which are known to stimulate osteoblast proliferation and differentiation [4]. 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 [7]. However, HA by itself has insufficient mechanical properties, especially low mechanical strength and increased brittleness. It is mainly applied in the form of bone fillers of several shapes for unloaded implants and in the form of a coating material on metallic prostheses, dental or maxillofacial applications [8]. Application of HA as composite matrix additives should overcome these problems. The rate of the interaction between the body and the artificial particles depends on their microstructure, morphology and size (e.g. nano/micro size).

The aim of our study was to perform an effect of matrix powder additives commonly used to increase the bioactivity on the behaviour of the composite potentially suitable for application as a filling material or as a substitute element in the human body. We are looking for a compromise between the optimum of amount fillers of the resulting composite and suitable mechanical properties. The aim of this study was just to describe the mechanical behavior and the changes in the structure of the composite (e.g. by image analysis and measurements), and also essentially the preparation of samples for subsequent in vitro biocompatibility testing (cytotoxicity, bioactivity testing).

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 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 the amount of 0, 2, 5, 10, 15, 20 and 25 vol% (powder/matrix). The ultimate strength in bending (R_{fM}) and the modulus of elasticity in bending (E_f) in the direction of the fiber axis were determined by a four-point bending set-up with the Inspekt 100 HT material tester (Hagewald & Peschke, Germany), in accordance with ISO 14125. Six samples from each group with dimensions of 60x7x2.2mm (length x width x thickness) were applied. An image analysis of the polished sections was performed using LUCIA software, ver. 4.8 (Laboratory Imaging, Inc., Czech Republic).

3. Results

The modulus of elasticity in bending (ultimate strength in bending)/HA (TCP) volume fraction relationships were determined (see *Figure 1 and 2*). Statistical analysis was carried out via nonparametric analysis of variance, at the significant level of 0.05 (Kruskal-Wallis

test, Mann-Whitney as post hoc test). Additions of nano powders in the range of 2 – 5 vol. % increase the strength in bending by 20 – 30 %. With further additions above 15 vol. % the strength in bending decreases slightly, and with 20 – 25 vol. % distinct cracks appear in the matrix. A similar course (with lower values of strength in bending) is observed when micro powders are added. It seems that the optimum amount of additives with both fillings is in the range of 10 – 15 vol. %.

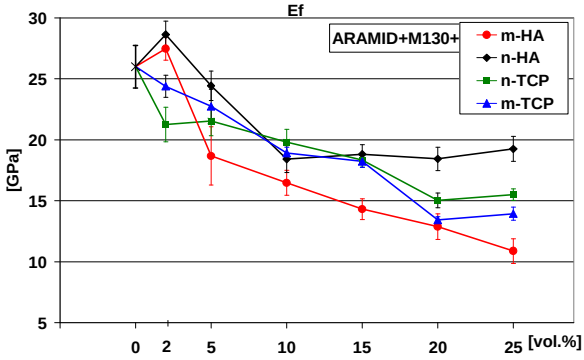

Figure 1: *Effect of nano and micro additives upon the modulus of elasticity in bending (Ef)*

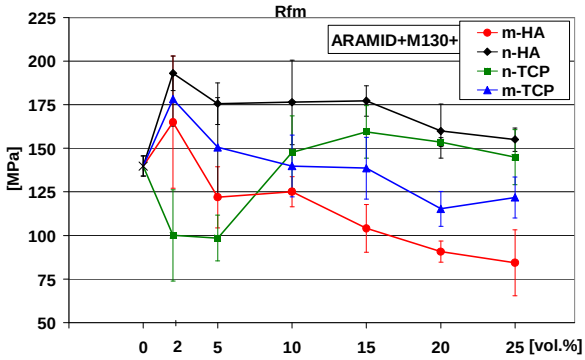

Figure 2: *Effect of nano and micro additives upon the ultimate strength in bending (Rfm)*

With the composites with both types of added powders, cracks (both horizontal and vertical) appear with volumes higher than 20 and especially 25 vol. %. A greater number of cracks can be observed on polished sections of composites added with micro powders (see *Figure 3, 4*). It seems that micro powders form aggregates in the matrix of the composites. These findings are ilustrated by the decrease of mechanical properties, especialy in the case of bending strength. Nano powders exhibit better dispersion with less frequent formation of aggregates (see *Figure 3 and 4*) leading in increase of bending strength. From the prepared polished sections we can draw the conclusion that the nano powders (both HA and TCP), with their better dispersion, are in closer proximity to the fibers. In general, we can state that the image analysis shows no distinct difference between the HA and TCP fillers: differences are visible only on micrographs with a different particle size of the fillers.

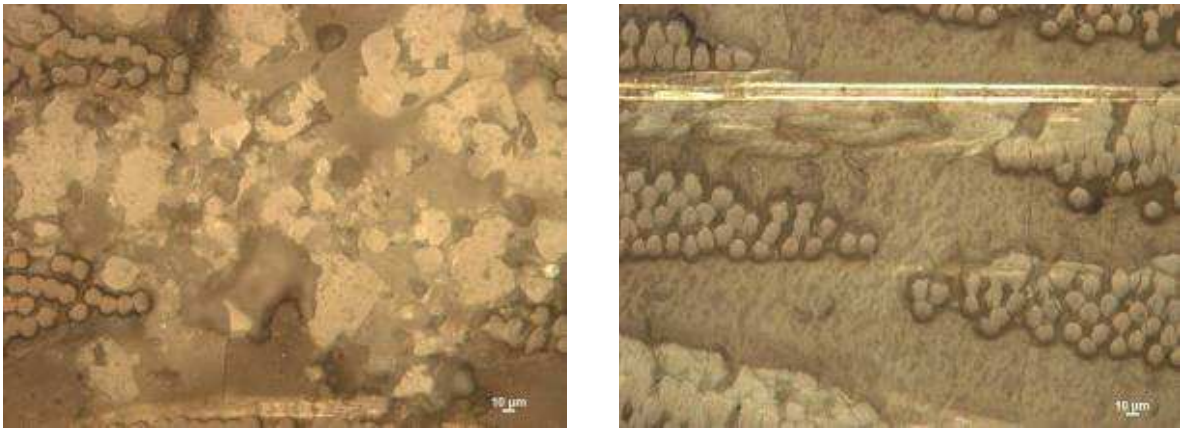

Figure 3: *Micrographs of polished sections of composite ARAMID+M130 added with micro and nano powders (left: m-HA, 20 vol. %, right: n-HA, 20 vol. %).*

4. Conclusions

This paper has investigated the effect of micro and nano particles on the mechanical properties of a fiber composite designed for applications in bone surgery. The aim was to find

and verify a suitable ratio of additives to optimize mechanical properties of composites to be comparable with that of the human bone. It has been shown that in general both the micro and nano fillers reduce the modulus of elasticity in bending. Bending strength increased by the addition of nano powders. Micro particles tend to produce a negative effect of bending strength decrease, which is probably due to their non-uniform dispersion in the composite matrix or due to the formulation of the aggregates. Addition of nano powders results in the possitive effect on the mechanical properties compare to micro particles. From the point of view of mechanical properties, the addition of 10 – 15 vol. % of nano particles appears to be the optimum amount with which a suitable optimization of the mechanical properties is achieved without any changes in the inner structure of the composite. The formation of cracks and aggregates with additive volumes above 20 vol. % could have a negative effect on the long-term properties of the composite, especially on the further propagation of cracks and on the fatigue strength. An analysis of the mechanical properties, and also the image analysis, show no fundamental difference between the HA and TCP fillers. In this paper, two different particle sizes (micro and nano) of the powder fillers were investigated with regard to their effect on the mechanical properties; further studies will deal with the effect of their size and quantity on their interaction with the bone tissue. It will be necessary to verify the effects of the composite material, its porosity and its individual components on the adhesion, growth, maturation, viability and potential immune activation of osteogenic cells in vitro. The influence of long-term storage in simulated body fluid on the chemical composition and mechanical properties of the composite will also be studied.

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