Polymer- ceramic nanocomposites for applications in the bone surgery

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Abstract. The subject of this work was preparation and investigation of properties of a nanocomposite material based on polymer matrix modified with nanometric silica particles (SiO₂). The composite matrix consisted of resorbable P(L/DL)LA polymer with certified biocompatibility. Nanometric silica was introduced into the matrix by means of ultrasonic homogenisation and/or mechanical stirring. The silica was introduced directly e.g. as nanoparticles or inside calcium alginate fibres which contained 3 wt.% of amorphous SiO₂. Proper dispersion of nano-filliers was confirmed by means of thermal analysis (TG/DTA, DSC). It was observed, that the presence of inorganic nanoparticles influenced several surface parameters of the nanocomposites i.e. hydrophility (a decrease of surface energy) and topography (both in micro- and nano-scale). Additionally, the nanocomposites exhibited enhanced mechanical properties (Young’s modulus, tensile strength) compared to the pure polymer. The nanocomposites were bioactive materials (SBF/3 days/37°C). Biological tests (MTT test) showed a good viability of human osteoblasts (hFOB 1.19) in contact with the nanocomposites surface. Results of preliminary biological tests carried out with the use of mother cells extracted from human bone marrow showed that the nanocomposites may provide differentiation of bone cells.

1. Introduction

Nanocomposites are materials which are recently more readily applied in biomaterials engineering [1]. Application of the nanocomposites may considerably contribute to a production of biocompatible, bioactive materials stimulating the reaction of repair cells. The another advantageous aspect of their application is a possibility to control resorption time of degradable or, bio-resorbable nanocomposites by adjusting an amount of a particular nano-fillier (e.g. TCP, MMT) [2,3]. It is well known, that one of the main factors limiting the application of some biocompatible polymers in bone surgery is their low strength. Nanocomposite materials for bone surgery applications are designed to be mechanically and chemically compatible with a substituting tissue. Interaction between nano-fillier and polymeric chains of the matrix leads to production of strong and flexible materials. Due to a possibility of an application of bioactive ceramic particles such as HA or SiO₂, the fabricated nanocomposites may be used for direct joining of bones [3]. Materials from this group induce specific biological reactions on tissue-implant interface which lead to the formation of bonding between an

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implant and a bone. It occurs due to a local supersaturation of immersing medium and enrichment of the nanocomposite superficial layer with calcium and phosphorus ions (when HA is a nano-filler), or a possibility of formation of O-Si-O bonds at a nanoparticle surface (when SiO$_2$ is a nano-filler) leading to nucleation of apatite. Moreover, due to a small required amount of the nano-modifier, the nanocomposites are lighter and cheaper than the conventional ones.

The aim of a present work was to produce and analyse properties of a polymer nanocomposite materials in which silica (SiO$_2$) nanoparticles were applied as a modifier. A matrix of the composites consisted of the resorbable P(L/DL)LA polymer. Nanometric dispersion of the nano-filler particles was confirmed by a thermal analysis and mechanical tests. The presence of the nanoparticles influenced hydrophilicity and surface topography of the nanocomposites. The fabricated materials were bioactive.

2. Materials and methods

The polymer used in the studies was poly(L-lactide-co-D,L-lactide) (Boehringer Ingelheim, Germany) in which L-lactide to D,L-lactide ratio was 80:20, and molecular weight 200 000 Da. The polymer matrix was modified with nanometric amorphous silica (a-SiO$_2$, Sigma-Aldrich), whose mean particle size was 5-10 nm. A second type of modifier was nanocomposite biopolymer fibres made of calcium alginate (Ca(Alg)$_2$) containing 3 wt.% of a-SiO$_2$. The fibres were fabricated using the wet shaping technique in the Department of Man-Made Fibres of Faculty of Textile Engineering and Marketing of Technical University of Lodz. The fibres before introduction into the polymer matrix were mechanically ground by means of the vibrating ball mill. The final form of the modifier consisted of two fractions i.e. short fibres (diameter to length ratio 1:10) and products of the fibres crushing i.e. fibre fractions and a-SiO$_2$ particles. Mean size of the fibres crushing products was about 220 – 300 nm (DLS, NanoSizer, Nano ZS, Malvern Inst.). Morphology of the modifiers is presented in Fig.1.

![Figure 1. Morphology of the modifiers; alginate fibres with 3% SiO$_2$ (A) and aSiO$_2$ (B).](image)

The polymer-ceramic composites were produced using the casting method. The polymer was dissolved in an organic solvent (dichlorometane) (1:10), then homogenised with the nanoparticles (0.5 wt.%) or the fractured alginate fibres (2 wt.%) by means of ultrasonic agitation and mechanical stirring and finally cast. As a result, thin composite foils were produced. In order to verify if the fabricated materials belonged to the nanocomposites group they were subjected to thermal analysis using the differential scanning calorimetry (DSC) in an inert gas atmosphere at temperatures from 50 to 600°C (DSC 2010 TA Instuments). For the same reason mechanical tests were performed in the tensile mode (measurement base – 15 mm) using the universal testing machine (Zwick 1453). In both cases the reference material was pure P(L/DL)LA foil. Topography of the materials was examined by means of profilometry (Hommerwelker T500), nanotopography was observed using the AFM microscopy (Digital Instruments).
Wettability of the composite materials surface was determined by a direct method (DSA 10, Kruss) using water (UHQ, Pure Lab) as a measuring liquid. Measurements were performed at room temperature. The surface energy was determined by the Owens-Wendt method using diiodomethane as a non-polar liquid. Bioactivity test was performed by incubation of all materials in simulated body fluid (SBF), which is an artificial body fluid with pH and ion concentration similar to the natural one, but free from cells and proteins (Table 1). Immersing samples for a given time in SBF (in vitro conditions) allows simulate in vivo conditions in which a layer of apatite forms at a material’s surface. The incubation lasted 3 days at 37°C. Microstructure of samples after the incubation was observed using SEM (JMS-400 JEOL).

Table 1. Composition of SBF – simulated body fluid

| Fluid    | Na⁺ | K⁺  | Mg²⁺ | Ca²⁺ | Cl⁻  | HCO₃⁻ | HPO₄²⁻ | SO₄²⁻ |
|----------|-----|-----|------|------|------|-------|--------|-------|
| plasma   | 142.0 | 5.0  | 1.5  | 2.5  | 103.0 | 27.0  | 1.0    | 0.5   |
| SBF*     | 142.0 | 5.0  | 1.5  | 2.5  | 148.8 | 4.2   | 1.0    | 0.5   |

3. Results and Discussion

Results of the mechanical tests proved, that fabricated composites are materials which behave like nanocomposites. According to the theory of conventional composites, the applied amount of the modifier (nano-filler) i.e. 0.5 or 2 wt.% should act as a defect which weakens the material. The carried out tests showed, that such weakening does not take place. In the case of both modifiers i.e. silica nanoparticles (0.5 wt.%), and the fractured alginate fibres (2 wt.%) Young’s modulus of the materials as well as their toughness (higher fracture energy) increased. From the point of view of composite materials, particularly interesting is the fact, that an increase of material’s toughness is caused by so small amount of fibrous phase. It is well known, that in a conventional composite material similar increase would take place if an amount of fibres was 50-56 wt. %.

During grinding of the alginate fibres some fraction of the silica nanoparticles fall out of them. Amount of a-SiO₂ particles introduced by means of the biopolymer fibre was c.a. 0.5 wt.%. The applied modification of PL(L/DL)A with the amorphous silica led to over three-fold increase of the Young’s modulus (Fig.2). This phenomenon may be related to a high specific surface area (about 580 m²/g) of a-SiO₂. Even when the amount of nanoparticles is small, during stretching of the material ordering of the polymer structure, and increase of the interaction force between the nanoparticles and the polymer chain took place.

Figure 2. Changes of Young’s modulus of composites samples.
Formation of a nanocomposite is accompanied with shifting of the material melting temperature towards lower values comparing to the pure polymer [5]. DSC analysis revealed, that the peak observed at DSC curves of the nanocomposites is shifted towards lower temperatures comparing to the maximum of pure polymer curve (Fig.3).

The presence of the nano-filer particles within the polymer matrix changed roughness of the material surface (topography) and physico-chemical properties of the material surface. SEM observations showed, that an introduction of alginate fibers and products of their crushing into the polymer matrix changed microstructure of the nanocomposite surface, so that it become irregular, and mapping shape of the fibrous phase (Fig.4).

Some amount of the fibres was not covered with a polymer layer. Results of profilometry measurements showed, that roughness of the nanocomposite modified with the calcium alginate fibres was in micrometer scale. The average level of the composite surface roughness ($R_a$) was 2.79 µm, while $R_o$ of the pure polymer surface was 0.24 µm, which is comparable to the a-SiO$_2$ nanocomposite for which $R_o = 0.29$ µm.
Type of the modifier strongly influences materials wettability. The applied amount of a-SiO$_2$ only slightly enhanced the materials hydrophilicity ($\theta=71^\circ$) comparing to the pure polymer ($\theta=75^\circ$). Introduction of the fibrous phase (and products of its crushing) decreased the wetting angle by 10$^\circ$ (Fig. 5). The total surface energy of the materials changed in accordance with the direction of wetting angle changes (Fig. 6). Introduction of the fillers caused increase of the polar component, which is responsible for the material hydrophility. This effect may have significant influence on the further behaviour of the material in in vitro conditions of a cell culture.

![Figure 5](image5.jpg) Changing of contact angle for composites materials and polymer folii

![Figure 6](image6.jpg) Changing of surface free energy for composites materials and polymer folii

After the incubation in SBF medium, at the nanocomposite materials surface structures typical for apatite appeared. EDS analysis of the structures revealed a presence of calcium and phosphorus atoms which are constituents of apatite (Fig. 7). The amorphous silica particles, which were present in both types of the nanocomposites, had a high specific surface area, which is probably a result of their microporosity. This may suggest, that number of silane groups (Si-O-Si) is relatively high which enables formation of bonds between the material and ions present in the medium. SBF medium contains calcium and phosphorus ions which are necessary for nucleation and crystallization of apatite.
Figure 7. SEM image of the surface of composite materials: PL(L/DL)A with 0.5% wt aSiO$_2$ after 3 days contact with SBF

Figure 8. SEM image of the surface of composite materials: PL(L/DL)A + 2% wt Ca(Alg)$_2$ with 3% wt. aSiO$_2$ (short fibres and products of degradation of fibres) after 3 days contact with SBF

4. Conclusion

The fabricated composite materials containing nanometric amorphous silica directly, or indirectly introduced into the resorbable polymer matrix are promising methods of formation of strong and bioactive nanocomposite implants destined for application in bone surgery e.g. for regeneration of bone defect.

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