Bioabsorbable polymer plates coated with bioactive glass spheres

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In order to provide bioabsorbable self-reinforced poly (L/DL) lactide (P(L/DL)LA) 70 : 30 plates with osteoconductive bioactivity, spheres (125–250 μm) of a bioactive glass 13–93 were implanted onto a polymer plate preform by pressing. With appropriate pressing parameters glass spheres were firmly attached onto the polymer plate. The top of the glass spheres remained exposed. The bioactivity of the coated plates was examined *in vitro* with immersion in phosphate-buffered saline (PBS). Apatite was observed to precipitate on exposed glass sphere surfaces and the whole polymer surface within the first three days.
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1. Introduction

Bioabsorbable polymeric implants, like self-reinforced polylactide (SR-PLA) pins, screws and plates, are widely used for temporary fracture fixation [1, 2]. Especially in craniomaxillofacial surgery bioabsorbable miniplates and screws are used to facilitate the fixation of bone fragments [3].

Uni- and biaxially oriented bioabsorbable polymer plates can be achieved by using solid-state deformation methods, like the self-reinforcing technique and compression molding, as developed by Törmälä's research group [4]. The tough, high-strength structure of the oriented and self-reinforced plates allow the *in situ* deformation of the plates at room temperature, for example in the operating theater prior to implantation.

To enhance bone tissue formation and to facilitate fracture healing we have developed novel bioabsorbable composite plates by coating bioabsorbable polymer plates with bioactive glass. As a coating layer we have used bioactive glass 13–93, which is able to form chemical bond with bone tissue. It is resorbable, biocombatible and osteoconductive. Moreover, because of the glass composition, it has a large working range which allows, for example, the manufacturing of fibers and spherical particles [5].

In the present study, bioactive glass spheres were implanted onto the surface of self-reinforced, oriented poly (L/DL) lactide plate, in order to obtain a plate material which is strong and tough, biocompatible, bioactive (osteopromoting) and bioabsorbable.

2. Materials and methods

2.1. Materials

The raw material for the bioabsorbable polymer plates was poly (L/DL) lactide 70 : 30, Resomer LR 708 (Boehringer Ingelheim, Germany), inherent viscosity approximately 6.0 dl g^{-1}.

Bioactive glass 13–93 spheres were produced by flame spraying. The glass composition was: 6 wt % Na_2O, 12 wt % K_2O, 5 wt % MgO, 20 wt % CaO, 4 wt % P_2O_5, 53 wt % SiO_2 [5]. The particle size distribution was 125–250 μm. The glass is commercially available from Abmin Technologies Ltd, Finland.

2.2. P(L/DL)LA plate preform

Non-reinforced P(L/DL)LA rods (diameter 4 mm) were extruded by using a Gimac single screw microextruder (Mac.gi, Italy) with screw diameter of 12 mm. The extrusion temperature was 221 °C. Uniaxial solid-state die-drawing was used to produce self-reinforced, oriented rods. The drawing temperature was 60–70 °C and draw-ratio approximately 3.5. Strong and tough P(L/DL)LA plate preforms (thickness 0.7 mm) were achieved by compression molding of the self-reinforced rods. Total compression time was 5 min, maximum temperature 85 °C and pressure 12 MPa.

2.3. Implantation of bioactive glass spheres

Bioactive glass spheres were spread over the P(L/DL)LA plate preform and implanted onto the preform by pressing between metallic plates. Different pressing parameters were studied. The studied pressing parameters were: pressing temperatures were varied from 60 to 90 °C, time between 20 s–2 min and pressure 2–10 MPa. The specimen surfaces were studied by a scanning electron microscope (SEM; Jeol T100, Japan) at an accelerating voltage of 15 keV. The samples were coated with a thin gold layer before examination in the SEM.

2.4. Short-term *in vitro* studies

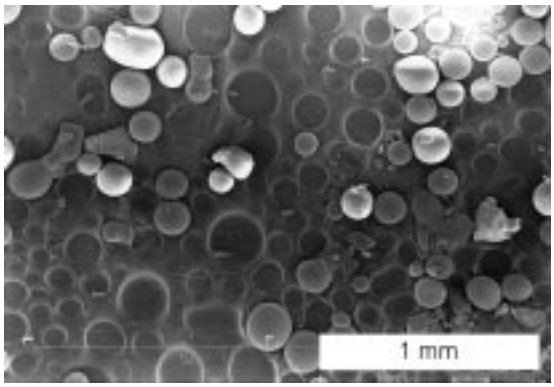
Hydrolysis behavior (apatite deposition) of the bioactive glass coating was studied in phosphate-buffered saline (PBS) at $37 \pm 1\,^{\circ}C$. Immersion times were 3 and 7 days. After immersion the specimens were rinsed with ultrapure water and ethanol, dried in a vacuum at 25 °C for 3 days and studied by SEM. The precipitation was analyzed by energy dispersive X-ray (EDX; EDAX, Philips XL 30, The Netherlands).

3. Results and discussion

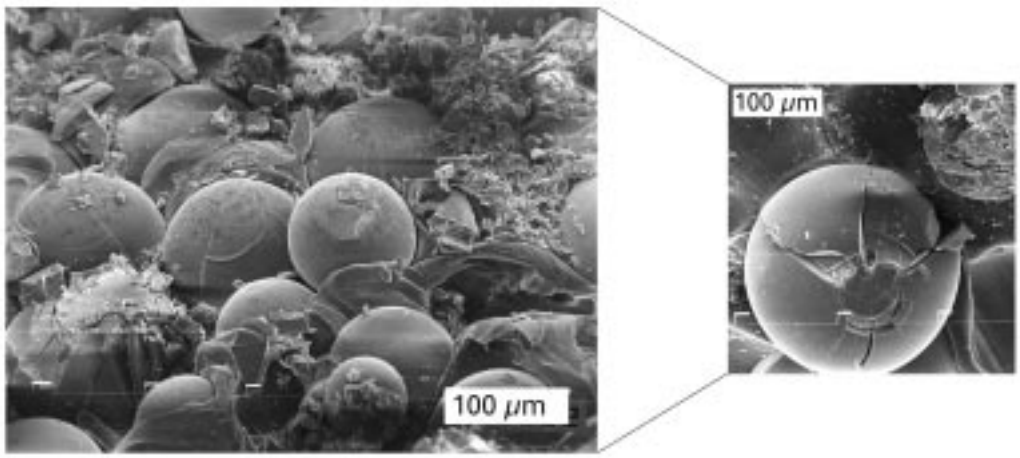
3.1. Surface characteristics

It was observed that the glass spheres were not attached to the polymer preform at pressures below 3 MPa, pressing times less than 1 min or pressing temperature below 80 °C (Fig. 1a). When the pressure was increased from 6 to 10 MPa, most of the glass spheres were crushed (Fig. 1b).

With increasing temperature to 85–90 °C, the spheres were totally sunk into the polymer preform. High temperatures also negatively affected the polymer orientation. With optimal pressing parameters (4 MPa, 80 °C, 2 min) bioactive glass spheres were firmly attached into the polymer preform and upper part of the spheres were exposed (Fig. 2). It was found that the glass spheres do not peel off during deformation of the plate at room temperature (Fig. 3).



(a)



(b)

Figure 1 Scanning electron micrographs of plates coated with bioactive glass spheres with pressing parameters: (a) 2 MPa, 80 °C, 2 min; (b) 10 MPa, 80 °C, 2 min.

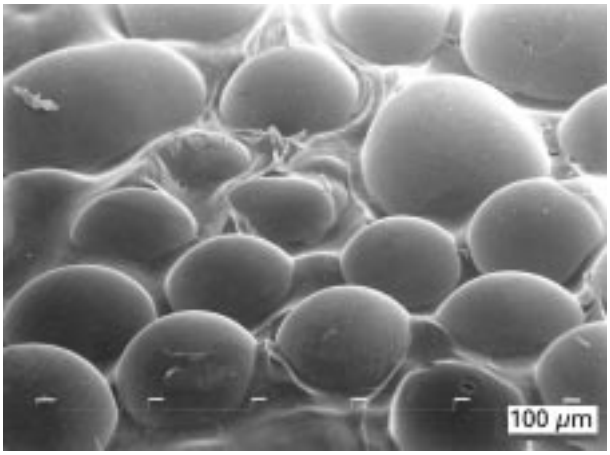


Figure 2 Scanning electron micrograph of a plate coated with bioactive glass spheres with pressing parameters 4 MPa, 80 °C, 2 min.

3.2. Surface hydrolysis behavior

Immediate contact of the glass with the hydrolysis buffer was achieved due to the exposed glass sphere surfaces. This allowed bioactive glass surface reactions to start as soon as the contact to the hydrolysis buffer was established. Short-term *in vitro* studies showed that the apatite precipitation is formed within the first 3 days. Apatite layer and resorption of a glass sphere can be observed in Fig. 4a. In addition, apatite precipitation was also formed on the polymer matrix adjacent to the glass spheres, making the bioabsorbable polymer surface attractive for bone tissue formation (Fig. 4b). EDX analysis of the precipitate indicated the existence of silicon, phosphorus and calcium. Our observation, about the rapid start, spreading of the glass reactions and formation of the apatite layer into the adjacent polymer is a novel one and may be an important step forward in the development of bioabsorbable, bioactive (osteopromoting) implant materials. Similar types of reactions have been seen earlier with bioactive glass–biostable polymer composites [6, 7]. However, because of exposed bioactive glass sphere surfaces, our composite material exhibits apatite precipitation rapidly without mechanical processing, such as grinding or cutting of the material to expose the glass phase, as was needed in the above cases.

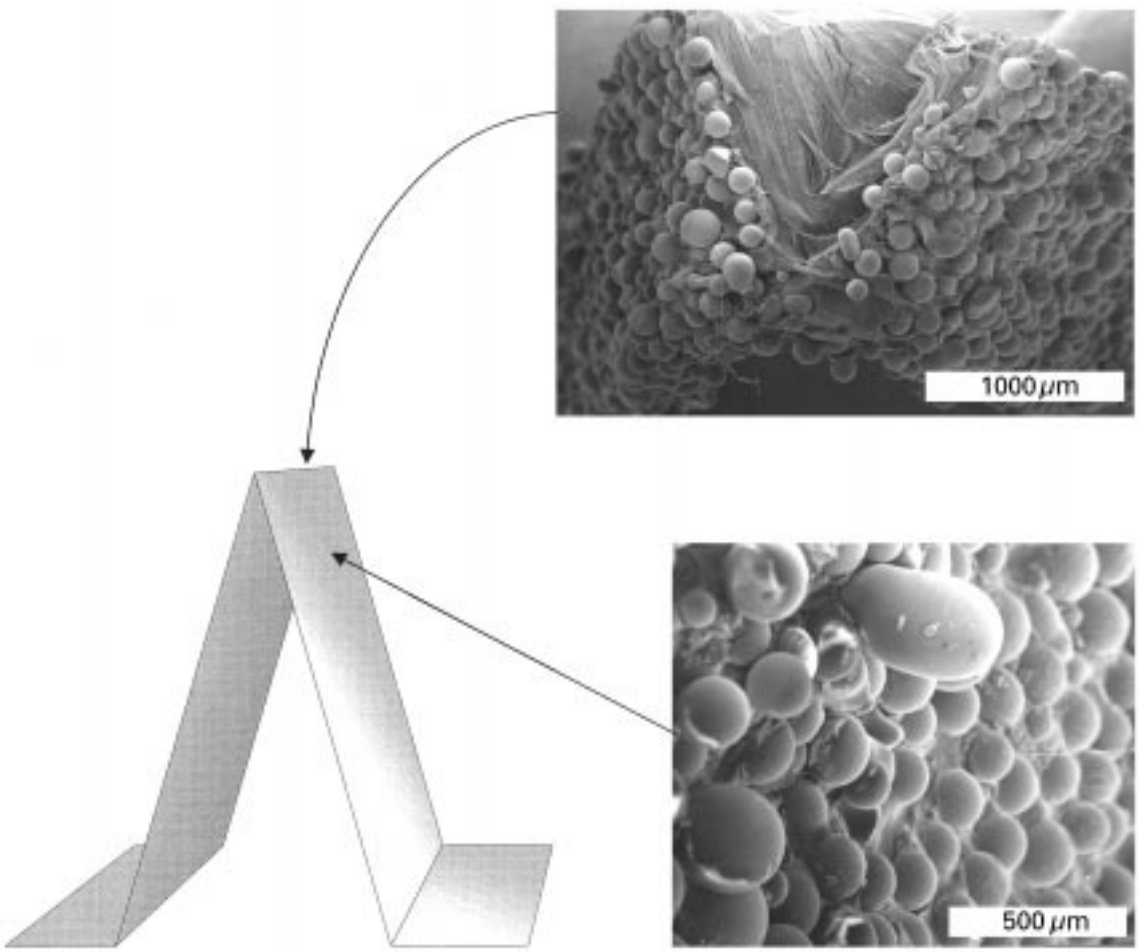


Figure 3 Scanning electron micrographs of a plate coated with bioactive glass spheres after vigorous plate deformation.

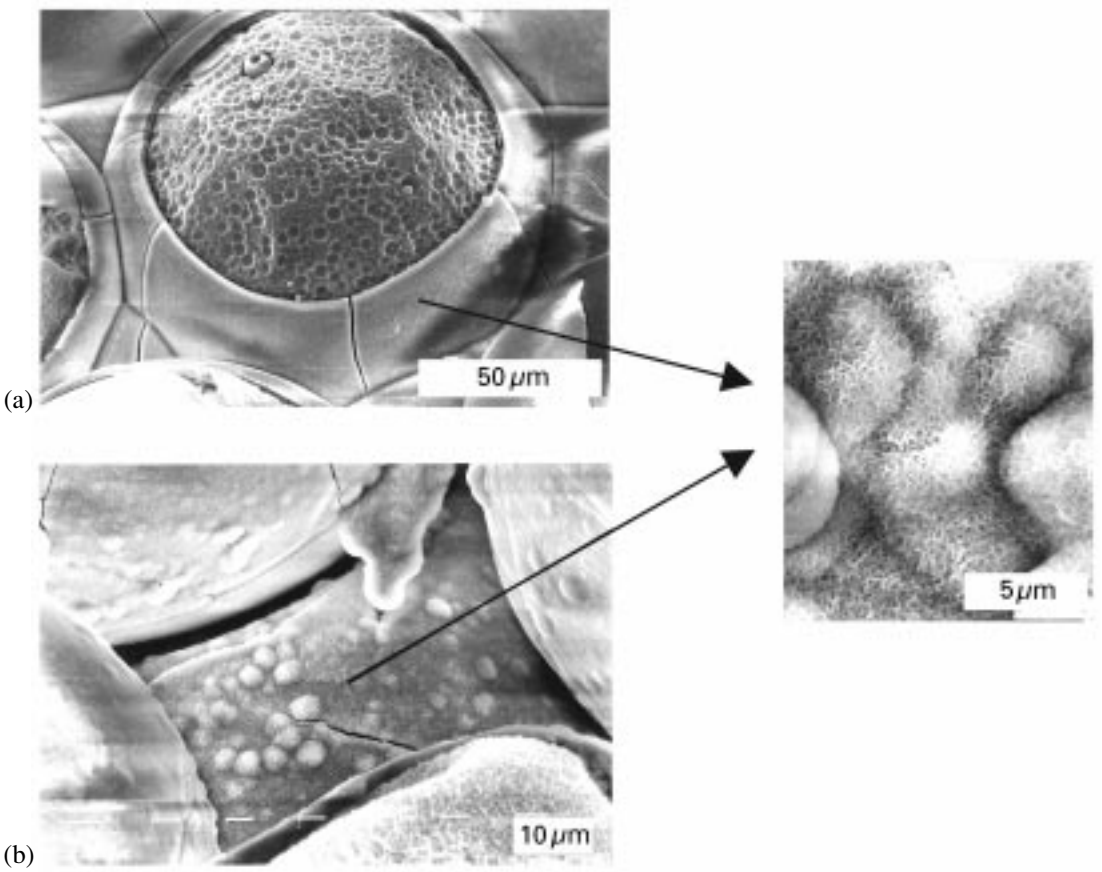


Figure 4 Formation of an apatite layer on the coated plate surface after 3 days in PBS: (a) glass sphere; (b) P(L/DL)LA matrix adjacent to glass spheres.

There is also a great difference between the polymer matrices used. We have used a bioabsorbable matrix compared to the other studies which were performed with biostable polymers.

4. Conclusions

We have shown that it is possible to implant bioactive glass 13–93 spheres onto the polymer preform surface by pressing. Precipitation of apatite was formed during 3 days *in vitro*, showing the bioactivity of the plates. We suggest that these novel bioabsorbable composite plates could be advantageously used for the fixation and repair of bone fractures and for guided bone regeneration.

Acknowledgment

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