THE EFFECT OF BIOACTIVE GLASS PARTICLE SIZE ON PROPERTIES OF POLY(ε-CAPROLACTONE) BASED MEMBRANES

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Introduction

The guide bone regeneration (GBR) involves application of barrier membranes to prevent soft-tissue ingrowth into the defect and to maintain a suitable space for bone regeneration process [1]. A membrane should actively promote bone formation and membrane-tissue integration that stabilizes the healing wound process [2]. It has been shown that the incorporation of bioactive glass (BG) particles into polymeric membranes can significantly enhance osteoblast proliferation and differentiation, indicating favourable osteoconductivity and/or osteoinductivity for GBR applications [1] and also can induce direct bone-material bonding [3].
The current study aimed to evaluate the effect of BG particle size (<3 μm, <45 μm) on properties of poly(ε-caprolactone) (PCL) membranes obtained by two methods, namely thermal-induced phase separation (TISP) and liquid-induced phase separation (LIPS).

Materials and Methods

BG particles with the composition of $40SiO_2$–$54CaO$–$6P_2O_5$ (mol%) were synthesized with the use of sol-gel method. PCL/BG membranes were prepared by TIPS and LIPS methods using 5%w/v PCL solutions in 1,4-Dioxane (DIOX) and N,N-Dimethylformamide (DMF), respectively. The assumed volume fraction of BG particles in composites was 21 vol.%. Both surfaces of films were evaluated in terms of surface properties: morphology (SEM), topography (confocal microscopy), wettability (contact angle goniometer). Also degree of crystallinity and melting point (DSC) of PCL were examined. *In vitro* bioactivity was assessed by incubation of materials in simulated body fluid (SBF) for 3, 7 and 14 days. The samples and incubation media were analysed with SEM/EDX, FTIR and ICP-MS methods, respectively.

Results and Discussion

The results showed that the use of BG particles of various sizes (<3 μm, <45 μm) affects surface properties such as morphology, topography and wettability; as well as *in vitro* bioactivity of the PCL/BG membranes obtained by two different methods.
In the case of materials obtained with LIPS method, the presence of BG particles in PCL matrix resulted in larger pore size in comparison with pure polymer membrane. However, material containing larger-sized particles (<45 μm) showed bigger pores than membrane with BG particles of <3 μm size. In turn, porosity and pore size of membranes, produced with TIPS method, decreased with the addition of glass particles into PCL matrix. Moreover, larger-sized particles (<45 μm) caused greater reduction in porosity and pore size.
The static water contact angle and water adsorption of membranes obtained with the use TIPS method were not affected by the presence of glass particles. On the contrary, the addition of BG particles of both sizes into membrane produced by LIPS method improved wettability and water adsorption. However, in the case of material containing glass particles of <3 μm size, more noticeable improvement was seen.

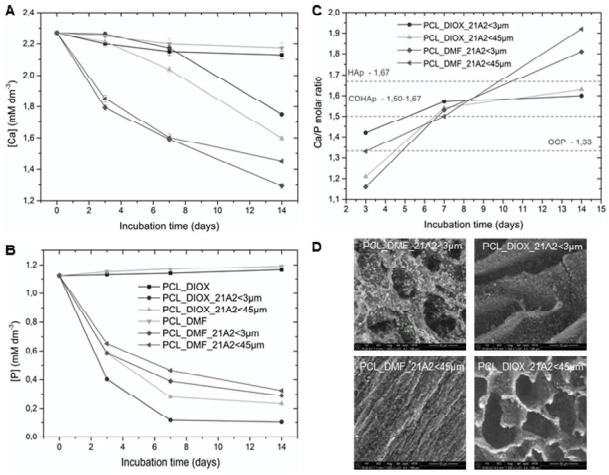

FIG. 1. Variations of the Ca (A) and P (B) concentrations in SBF during material soaking; Ca/P molar ratio (C) of the formed layer after material incubation in SBF; SEM images (D) of the materials after 14-day incubation in SBF.

All of the polymer membranes showed no significant changes in surface morphology and chemical composition after soaking in SBF. In turn, the surfaces of PCL/BG materials were fully covered with the thick layers rich in calcium and phosphorus (FIG. 1D). All of the layers exhibited spherical cauliflower-like morphology, typical of carbonated hydroxyapatite (HCA), as was additionally confirmed with FTIR spectroscopy. The results of Ca and P concentration in SBF during material soaking (FIG. 1A-1B) and also Ca/P molar ratio of the formed layers (FIG. 1C) indicated that kinetics of *in vitro* precipitation of HCA depends on both membrane preparation method and BG particle size. It was shown that after 7 days of incubation, for all composite materials, Ca/P molar ratio is characteristic of calcium-deficient HAp (CDHAp). However, after 14-day incubation, materials obtained by TIPS still show Ca/P ratio characteristic of CDHAp, while membranes produced with the use LIPS exhibit Ca/P ratio above value typical for Hap, which can indicate the formation of B-type carbonate-substituted hydroxyapatite (PO_4^{3-} substituting a tetrahedral group with CO_3^{2-}).

Conclusions

The results indicate the possibility of using various membrane preparation methods and also BG particles of different sizes to obtain materials with various, but controlled surface properties, as well as *in vitro* bioactivity.

Acknowledgments

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