IMPACT OF ZrO_2 ADDITIVE ON PROPERTIES OF PMMA-BASED BONE CEMENT

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Introduction

Bone cements have been widely used in medicine for over 50 years mainly for fixation of the prostheses and for filling up small bone cavities in maxillofacial area or in spine vertebrae. There are two major types of bone cements commercially available – acrylic bone cements made out of poly(methyl methacrylate) and calcium phosphate cements (CPCs). PMMA-based cements are implemented because of their satisfactory mechanical properties, low toxicity, low cost and easy mass production [1]. CPCs are bioresorbable and biocompatible but they exhibit low mechanical strength [2].

PMMA-based bone cements are formed by mixing two components – solid part and liquid part. The basic solid component consists of poly(methyl methacrylate), benzoyl peroxide – an initiator and zirconium dioxide (ZrO_2) or barium sulphate ($BaSO_4$) – a radiopaque. The liquid phase involves methyl methacrylate (monomer), hydroquinone – a stabilizer, and N, N-dimethyl-p-toluidine – an accelerator. All mentioned ingredients are added to provide efficient polymerization at room temperature.

Zirconium dioxide (ZrO_2) can be considered for reinforcement phases in bioimplants because of its biocompatibility, exceptional oxidation resistance and wear resistance [3].

This paper presents the effect of zirconium dioxide (ZrO_2 = 6, 12, 21, 30 wt%) on physical, chemical and mechanical properties of novel PMMA-based bone cements.

Materials and Methods

Composite bone cement samples were prepared by mixing following components in solid phase – Duracryl (copolymer of methyl methacrylate and methyl acrylate), benzoyl peroxide, zirconium dioxide and the liquid phase – methyl methacrylate stabilized with hydroquinone and N, N-dimethyl-p-toluidine. The amount of ZrO_2 was variable in the sample types, from 6wt% to 30wt%.

The surface morphology of the bone cements was examined on JSM-6610LV Scanning Electron Microscope. For the studies of the chemical composition of the samples, Nicolet IS 50 FT-IR Spectrophotometer was used. Additionally, the wettability was measured via sessile drop method. Contact angles were measured with KRUSS Contact Angle Measuring Instrument and surface free energy (SFE) was determined according to the Owens-Wendt method [4]. Thermal properties were evaluated by means of two techniques – thermal gravimetric analysis (TGA, PI Instrument) and differential scanning calorimetry (Mettler Toledo DSC1). Moreover, mechanical properties were examined – Indentation hardness of the specimens was determined by means of durometer (Shore hardness scale D) according the norm ISO 868:2003, and Charpy impact tests were done.

Results and Discussion

The morphology of the samples showed that ZrO_2 tends to agglomerate. The higher content of ZrO2, the greater difficulty to obtain homogenous structure without defects.

In the FTIR spectra signals from matrix polymer bonds and groups present in ZrO_2 were recorded. The characteristic peaks for the Zr—O bond were found at 750cm^{-1}, 610cm^{-1} and 430cm^{-1}. Additionally, the peak at 460cm^{-1} and 700cm^{-1} exhibited higher intensity when ZrO_2 was added to the samples, which was the result of interaction of C-O-C bonds in the polymeric matrix.

Surface Free Energy was quite similar for all samples regardless of amount of ZrO_2 (SFE = 59.5±3.5 mJ/m^2; polar component = 16.2±2.7 mJ/m^2; dispersive component = 43.4±0.8 mJ/m^2).

The character of the degradation of the samples was evaluated via TGA analysis. The higher amount of ZrO_2, the higher temperature of initial and final degradation. For 6wt% of ZrO_2 10% degradation of initial sample mass was found at 272°C, for 30wt% – 294°C.

Polymerization heat was checked in the samples. For samples with 0, 6, 12 and 21% ZrO_2 no significant differences were found. With 30% ZrO_2 the polymerization heat decreased by 7J/g to 53J/g.

Addition of 21% and 30% ZrO_2 in the samples improved their hardness compared to the sample without ZrO_2. The smaller amount of additive worsened this property. ZrO_2 inclusion in PMMA-based bone cements had negative effect on their toughness, however, the correlation was not found. Further investigation is needed.

Conclusions

Addition of zirconium dioxide (ZrO_2) has an impact on final material properties. ZrO2 plays important role as radiopaque in bone cements but also it can improve implanted biomaterial. The higher amount of zirconium dioxide allows to improve the thermal behaviour of PMMA-based bone cements and to adjust mechanical properties in final cement.

References

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