Water resistance of bone-cements reinforced with bioceramics

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Abstract

The water absorption behavior of bone-cements of PMMA reinforced with 1.5 wt.%, 2.5 wt.%, and 3.5 wt.% silane-treated powders of hydroxyapatite (synthetic, or derived from bovine bones, or teeth enamel), β-tricalcium phosphate (TCP), bioactive glass (45S5), and zirconia, was investigated. The experimental results showed that addition of calcium phosphate in the polymeric matrix favors water absorption except in the case of enamel hydroxyapatite. Water uptake is also suppressed when 45S5-bioglass or zirconia is added. The solubility is not affected by addition of hydroxyapatite or 45S5-bioglass but it increases when β-TCP or zirconia is added. A superior behavior of bone-cements reinforced with bioglass-45S5 and enamel hydroxyapatite can be suggested.

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1. Introduction

Acrylic bone-cements (BCs) of polymethylmethacrylate (PMMA) have been in use for more than forty years in orthopedic surgery as well as in dental implantology for expansion of dental implants [1,2], at maxillofacial prosthesis as gentamicin loaded beads [3,4], and at prosthetics for fixing partial dentures [5]. Since BCs are mechanically weak and not bioactive, in this study we experimentally investigated the possibility of reinforcing BCs with bioceramics. Bioactive ceramics and glasses favor formation of hydroxyapatite (i.e. the principal mineral of bones and teeth) when they come in contact with body substances after implantation.

Hydroxyapatite (HA, Ca10(PO4)6(OH)2) can be produced either chemically or from natural resources, such as from corals via hydrothermal transformation, or from bones of humans or (preferably) animals [6,7], or from enamel (EHA) or dentine (DHA) of teeth. The production of HA from bovine bones (BHA) without or with sintering at temperatures above 1000°C

| Table 1 Chemical composition of CMW™3, given by the manufacturer |
|-------------------|--------------------------|
| **Powder**        |                          |
| Polymethylmethacrylate (% w/w) | 88.00                |
| Benzoyl peroxide (% w/w)            | 2.00                   |
| Barium sulphate (% w/w)             | 10.00                  |
| **Liquid**        |                          |
| Methyl methacrylate (% w/w)        | 97.50                  |
| N,N-dimethyl-p-toluidine (% w/w)    | ≤2.50                  |
| Hydroquinone (ppm)                  | 25                     |

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has been described [8]. It has been also proposed that combination of HA with other phases in structures of composite materials can resolve the problem of high brittleness of HA [9].

For reinforcing, however, aims, ceramics already used in load-bearing biomedical applications, such as zirconia [10], can be also suggested, since they exhibit high strength and fracture toughness, but bioactivity remains as a question mark. Therefore, except HA itself, ceramics, such as the resorbable tricalcium phosphate ($\beta$-TCP, Ca$_3$(PO$_4$)$_2$) [8,11], or bioactive silicate glasses [12] (e.g. bioglass-45S5), which feature biocompatibility and osteoconductive and bone-bonding properties [13], can be also suggested for reinforcing BCs.

This paper presents the results of water resistance of reinforced BCs which we produced by incorporating in the polymeric matrix of PMMA bioceramics, specifically BHA, synthetic HA, $\beta$-TCP, bioglass-45S5, EHA reinforced with 10% zirconia (t-ZrO$_2$ stabilized with 3% yttria), and t-ZrO$_2$. The experiments comprised measurements of water absorption and weight loss after immersion of appropriately prepared samples of BCs in water. To achieve mechanically strong adhesion at the interface between the inorganic filler (bioceramics) and the polymeric organic matrix (PMMA) in the BC-composites, the surfaces of the bioceramics were subjected to silane treatment.

2. Materials and experimental procedure

To make this study realistic, in terms of the possibility of producing biomaterials in a large and global scale, the materials used (and consequently their purity) were of what can be commercially found in the open market of chemicals, regularly used to produce dental prosthesis, with respect also to the low production cost and the standard quality.

The production of BHA from femoral bovine bones [14], bioglass-45S5 [15], and EHA-ZrO$_2$ [16] has been described in earlier studies. Fine powders of synthetic HA, $\beta$-TCP, and t-ZrO$_2$ (3% yttria stabilized) were obtained from Merck A.G. (Germany). PMMA pre-polymerized powder (average particle size of 40 $\mu$m) and methyl methacrylate (MMA) liquid were purchased from IMICRYL (Turkey). General Electric (USA) supplied $\gamma$-methacryloxy-propyl-trimethoxy-silane (A-174). As a reference material for the experiments, CMW™3 bone-cement (DePuy, UK) was chosen, whose chemical composition is shown in Table 1.

The procedure of silanation and the preparation of BCs have been described in an earlier study [17]. In brief, the ceramic powders were sieved and the fraction below 100 $\mu$m was used. The silane coupling agent (0.2 wt.% with respect to the ceramic powders) was added in 100 ml of distilled water and the pH was maintained at 2.9. The powders of the ceramics were added to the solution and mixed at 50 °C with stirring at 350 rpm for 2 h (Velp Arex, Italy). The mixtures were dried at 110 °C for 5 h (Instron, USA). Table 2 lists the tested groups of this study. According to that table, an appropriate amount of silane-treated ceramic powders (i.e. 1.5%, 2.5%, and 3.5%) was added to PMMA powder. PMMA powder and MMA liquid were manually mixed at a ratio of 2.5/1.5. The reference CMW™3 BC was prepared according to the instructions given by the manufacturer.

The experimental procedure for measuring the water resistance of the produced BCs followed the standard test method for water absorption of plastics ASTM D 570–98 [18]. To prepare samples according to that standard, i.e. 50.8 mm in

![Fig. 1. Weight increase (%) during immersion in water (W in.%)](image-url)
diameter and 3.2 mm in thickness, a special mould of 304 stainless-steel was fabricated. Prior to sample preparation, the mould was heated up to 45 °C. Three samples from each group of Table 2 were tested. The samples, after conditioning, whereby they dried in air in an oven at 105 °C for 1 h, were immediately weighted \( W_{\text{con}} \). Then, they were immersed in distilled water for 120 min (±4 min) at 23 °C (±1 °C). Then, the samples were removed from the water, their surface was well wiped off with a dry cloth, and they were weighed \( W_{\text{wet}} \). The % of weight increase \( (W_{\text{in}}\%) \) was calculated by Eq. (1):

\[
W_{\text{in}}\% = \left( \frac{W_{\text{wet}} - W_{\text{con}}}{W_{\text{con}}} \right) \times 100
\]

Then, to calculate the soluble matter lost during the immersion in the water, the samples were reconditioned at the same conditions as above (i.e. 105 °C, 1 h) and immediately weighed \( W_{\text{reb}} \). The % of soluble matter lost during immersion \( (W_{\text{sol}}\%) \) was calculated by Eq. (2):

\[
W_{\text{sol}}\% = \left( \frac{W_{\text{reb}} - W_{\text{con}}}{W_{\text{con}}} \right) \times 100
\]

The accuracy (±) of weight measurements was 0.0005 g and of the “%” calculations 0.005%.

3. Results and discussion

An earlier study [17] has presented the experimental results of mechanical strength of BCs reinforced with silane-treated BHA, HA, and \( \beta \)-TCP (i.e. the groups A, B, and C). The experimental results of the present study integrate those of a previous study [17] by providing results of weight increase \( (W_{\text{in}}\% \), Fig. 1) and the soluble matter lost during immersion in water \( (W_{\text{sol}}\% \), Fig. 2) for the BC-composites of the groups A, B, C, together with the BCs of the groups D, E, F. The behavior (i.e. the values of \( W_{\text{in}}\% \) and \( W_{\text{sol}}\% \)) of pure PMMA (group G) and the standard CMW™3 is quite similar. Putting those values as a standard measure for comparison, it seems that the groups A, B, and C exhibit higher values of \( W_{\text{in}}\% \), and the groups D, E, and F lower ones (Fig. 1). Accordingly, the addition of calcium phosphate in the matrix of PMMA, in the form of either synthetic HA, or from bovine origin (BHA), or \( \beta \)-TCP, seemingly favors water absorption in the BC. Nevertheless, the BCs doped with enamel HA (group E) clearly deviate from that general trend, especially at low concentrations (E1 1.5% and E2 2.5%). It is known, however, that enamel contains F crystallized in fluorapatite (FA), and FA is more chemically resistant than HA. Hence, the combination of EHA with zirconia, which also suppresses water absorption (group F), results in those low values of \( W_{\text{in}}\% \) for group E. Low water absorption was also measured for the BCs doped with 45S5-bioglass particles.

As far as the amount of soluble matter is concerned \( (W_{\text{sol}}\% \), Fig. 2), it seems that HA (groups A and B) is quite resistive in water (comparing to the group G and CMW™3). The high solubility of \( \beta \)-TCP likely caused the higher values of \( W_{\text{sol}}\% \) of group C. The opposite was observed in the case of doping with EHA (group E), likely due to the high chemical resistance of FA in enamel. The particular bioactivity mechanism of 45S5 bioglass, which comprises ion exchange and surface structural transformations, seemingly resulted in negligible mass loss of the samples of group D. Finally, zirconia (group F) seems to increase the vulnerability of the BC-composites towards water.

There is no evidence of a systematic influence of the amount of the additives on the values of \( W_{\text{in}}\% \) and \( W_{\text{sol}}\% \), taking also into account the error bars of the mean values plotted in the two diagrams of Figs. 1 and 2. Hence, a different impact of each bioceramic to BCs may be suggested, with regard to water resistance.

Kim et al. [19] have measured water absorption and weight loss of three different BCs reinforced with 40%, 50%, and 60% HA derived from porcine spines and also doped with 10% chitosan, in physiological saline after 8 weeks. They observed that \( W_{\text{in}}\% \) and \( W_{\text{sol}}\% \) temporarily increase with increasing HA amount.

To conclude the potential of the investigated BCs in biomedical practice, the experimental results of this study must be correlated to the mechanism of expressing bioactivity for each particular BC-composite. For instance, if a phosphate-containing material dissolves very quickly, then it may cause irritation to the tissues in the implant’s neighborhood. Therefore, the kinetics of dissolution must match the biological reactions and the rates of tissue regeneration. Although such an explicit analysis is beyond the scope of this brief communication, we can generally suggest that the higher \( W_{\text{in}}\% \) values imply more microorganisms accommodated in an increasing porosity inside the bulk of the implant, which also increase the possibility of mechanical failure of BC during the functional time. Hence, the experimental results of this study suggest a superior behavior of the BC reinforced with bioglass-45S5 and EHA suitably doped with zirconia. The role, however, of zirconia as dopant of EHA regarding its solubility must be further investigated.

4. Conclusions

Six different types of PMMA bone-cements (BCs) doped with different biocompatible ceramics and glasses were produced and tested towards their water resistance. The
experimental results showed that addition of calcium phosphate in the matrix of PMMA favors water absorption of BC, except in the case of EHA. Water uptake is also suppressed when 45S5-bioglass or zirconia is added. The solubility of BCs is not affected by the addition of HA, BHA, EHA, or 45S5-bioglass, but it increases when β-TCP or zirconia is added in PMMA. The BCs reinforced with bioglass-45S5 and EHA-zirconia exhibited a superior behavior among the investigated BCs.

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