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Abstract

AIM: To engineer systems using polyisoprene (PI) or polycaprolactone (PCL) and nanometric bioactive glass 45S5 (BG) that could create a hydroxyapatite interface and thus ultimately make the use of an endodontic sealer unnecessary. METHODOLOGY: Different composites using PI or PCL as matrix material were prepared with BG contents of up to 30 wt%. Unfilled PI and PCL, commercially available filled PI (Obtura gutta-percha) and PCL pellets (Resilon) served as control materials. Bioactivity (in vitro precipitate formation in simulated body fluid) was investigated using scanning electron microscopy and X-ray diffraction analysis. To test immediate sealing ability, simulated root canals were filled with heated materials, and dye leakage was assessed. Leakage was statistically compared between groups using Kruskal-Wallis analysis of variance followed by Mann-Whitney U tests and Bonferroni correction. The alpha-type error was set at 0.05. RESULTS: Both composite systems revealed hydroxyapatite formation on their surface. This was not observed on control materials. Incorporating 30 wt% BG into PI and PCL significantly ($P < 0.05$) improved their immediate sealing ability compared to that of unfilled polymers, so that dye leakage in simulated root canals was prevented completely. CONCLUSION: Polyisoprene and PCL composites with BG showed promising results as single root canal filling materials. Incorporation of BG fillers into the polymers under investigation made the resulting composite materials bioactive and improved their immediate sealing ability.

Composites made of flame-sprayed bioactive glass 45S5 and polymers: bioactivity and immediate sealing properties

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Key words: bioglass, gutta-percha, nanoparticles, root canal, sealer

Short title: Bioactive root fillers

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Results Both composite systems revealed hydroxyapatite formation on their surface. This was not observed on control materials. Incorporating 30 wt% BG into PI and PCL significantly ($P < 0.05$) improved their immediate sealing ability compared to that of unfilled polymers, so that dye leakage in simulated root canals was prevented completely.

Conclusion PI and PCL composites with bioactive glass showed promising results as single root canal filling materials. Incorporation of bioactive glass fillers into the polymers under investigation made the resulting composite materials bioactive and improved their immediate sealing ability.

Introduction

The basic concept of filling root canals has not changed over the past 80 years (Bellizzi & Cruse 1980). In the age of biomaterials, there is still a lack of novel materials based on so called "biological substances" in the fast evolving world of endodontology. It has been believed that a root filling should be biocompatible and thus inert (Gatewood 2007). However, proper disinfection is a goal that is difficult to achieve (Nair *et al.* 2005), and consequently, some antimicrobial effect of a root filling material may be desirable. Currently, gutta-percha (filled polyisoprene, PI) has been the gold standard root filling material for almost a century (Bellizzi & Cruse 1980). A few years ago a new material based on polycaprolactone (PCL) was introduced (Resilon, Pentron, Wallingford, CT, USA). With both, materials based on either PI or PCL, a so-called sealer is necessary because they do not bind to the root canal wall (Gatewood 2007). However, whilst the core materials are relatively biocompatible (Sjogren *et al.* 1995), sealers irritate tissue (Yesilsoy *et al.* 1988, Gencoglu *et al.* 2009).

A recent publication has challenged the current concept of filling root canals (Alani *et al.* *f*2009). A PCL/phosphate glass composite was heated and then filled into root canals of extracted human teeth. The material showed handling properties similar to those of commercially available core materials used for root filling. However, the PCL/phosphate glass sealed root canals in a humid environment without the application of any sealer. This was related to the bioactivity of the material, i.e. its ability to form hydroxyapatite precipitates on its surface upon exposure to simulated body fluid (SBF). However, PCL may not be the best matrix material to be used as root filler, because it degrades over time

and thus looses its sealing ability (Paque & Sirtes 2007, De-Deus *et al.* 2008). It is conceivable that PI, the matrix material contained in gutta-percha, could provide a better long-term seal. Furthermore, phosphate glasses, whilst bioactive, do not display any disinfecting capacity. Bioactive glasses of the SiO_2-Na_2O-CaO-P_2O_5 type have antimicrobial properties (Stoor *et al.* 1998, Zehnder *et al.* 2004), which are based on their release of alkaline species (Gubler *et al.* 2008). This effect is enhanced in the presence of dentine (Zehnder *et al.* 2006). In theory, these materials are ideal root canal fillers, because they transform from initially alkaline biocides into inert calcium phosphate. However, SiO_2-Na_2O-CaO-P_2O_5 glasses are unable to prevent bacterial leakage through root canals if administered as aqueous suspensions (Zehnder *et al.* 2007). Conceivably, this is because bioactive glass has no primary sealing capacity, and the formation of precipitates that may hinder leakage takes time (Sepulveda *et al.* 2002). As has been shown (Alani *et al.* 2009), the conjunction of a bioactive glass with a suitable matrix material could provide an immediate seal that could later be enhanced by the formation of Ca/P precipitates at the naturally humid dentine-to-root filling interface (Papa *et al.* 1994).

It was the goal of the present investigation to devise composites of either PI or PCL with flame-sprayed bioactive glass 45S5. These composites were tested for their *in vitro* bioactivity by scanning electron microscopy and X-ray diffraction analysis. Dye penetration in simulated root canals was used to assess the potential of preventing immediate coronal leakage. Pure PI and PCL and commercially available Resilon and gutta-percha pellets were used as controls.

Materials and Methods

Bioactive glass and composites

Nanosized bioactive glass (BG) particles were produced as described in detail earlier (Brunner *et al.* 2006). Briefly, hexamethyldisiloxane (ABCR, Karlsruhe, Germany), calcium 2-ethylhexanoate (5.52 wt% Ca), sodium 2-ethylhexanoate (5.11 wt% Na) and tributylphosphate (Sigma-Aldrich, Buchs, Switzerland) were mixed and diluted with xylene to a final metal precursor concentration of 0.8 mol L^{-1}. The precursor was fed (10 mL min^{-1}) through a capillary (0.4 mm) dispersed with oxygen (10 L min^{-1}) and ignited with a methane (1.13 L min^{-1})/oxygen (2.4 L min^{-1}) flame. The particles were collected on baghouse filters and sieved subsequently. Polycaprolactone (PCL) and trans-polyisoprene (PI), the raw material of gutta-percha, were obtained from Sigma-Aldrich (Buchs, Switzerland). Composite specimens were produced via a two-step process, i.e. solvent casting and hot pressing (Borbely *et al.* 2008). The BG particles (max. 3 wt% with respect to the solvent) were dispersed in chloroform with an ultrasonic processor (UP400S, Hielscher, Teltow, Germany) at 320 W for 5 min with pulsed Intervals (50%). Corresponding amounts of PCL or PI were added afterwards and continuously stirred overnight. The solution was cast into glass dishes and the chloroform evaporated during 24 hrs at room temperature. Samples of a uniform size (20 x 3 x 0.5 mm) were prepared using a hot press at 75 °C and 44 kN. The obtained specimens were used for a short term *in vitro* bioactivity study and a leakage test (see below).

Gutta-percha (Obtura, Shoreline, CT, USA) and Resilon (Pentron) pellets were used as commercial reference materials, which contain PI and PCL, respectively. Pure PI and PCL specimens were used as further controls.

Scanning electron microscopy (SEM) images were taken on a LEO 1530 Gemini (Zeiss, Oberkochen, Germany) after sputtering the samples with ~4 nm of platinum to observe the distribution of the BG particles in the composites and to compare them to Resilon and gutta-percha samples. Static contact angle measurements were performed on dry films to determine the wettability and the hydrophilicity of test and control materials. Five measurements per sample were carried out at ambient temperature using a goniometer (NRL C, Ramé-hart Inc., Mountain Lakes, NJ, USA). Water droplets (ultrapure) with a volume of 4 μL were used for each measurement.

In vitro bioactivity

The bioactivity of the composite blocks (triplicates) was tested using freshly prepared simulated body fluid (SBF) filtered through a Nalgene® pre-sterilized filter unit (Kokubo *et al.* 1990). Hot pressed composite blocks and reference samples were weighed (M_0), dipped in ethanol to avoid bacterial contamination, dipped in Millipore water and finally placed in SBF at 37 °C for up to 28 days. To maintain a constant ion concentration SBF was exchanged every 7 days. The weight change was measured by rinsing with Millipore water and wiping, and recording the dry weight (M_d) after drying the samples in vacuum for 48 hrs. The weight change (WC) was calculated according to the following equation.

$$WC = \frac{M_0 - M_d}{M_0}$$

Surface examination of composite blocks before and after soaking in SBF can show the formation of carbonated hydroxyapatite. This formation is an indicator for *in vitro* bioactivity of biomaterials and can potentially create an improved seal because of a barrier function in the wet environment of a root canal (Alani *et al.* 2009). Precipitate formation was visualized using SEM. X-ray diffraction (XRD) patterns were recorded on a X'Pert PRO-MPD diffractometer (CuKα radiation, X'Celerator linear detector system, step size of 0.033°; PANalytical, Netherlands) at ambient conditions. Blind experiments using thermogravimetric analysis (TGA/SDTA851e, Linseis, Germany) were used to test the inorganic content of the specimens before and after immersion in SBF.

Immediate leakage test

A dye penetration test was carried out to check whether the investigated composite systems could prevent immediate coronal leakage. Standardized training blocks (Thermafil Training Bloc, Dentsply Maillefer, Ballaigues, Switzerland) were cut to obtain a single canal and the lateral canals were plugged with wax (Fig. 1a). The Obtura II heated gutta-percha system (Obtura, Fenton, MO, USA) with a 26-gauge applicator needle was used to fill the simulated canals (Fig.1b, c). Root fillings were made by a professional endodontist. A backfill procedure was performed in one step without any pluggers. PI and gutta-percha samples were filled with the Obtura System set at 200 °C, Resilon with 160 °C and PCL with 120 °C. Six canals per group were filled and the training blocks were stored at room temperature for 6 hrs. Subsequently, 8-10 µL of Royal Blue ink (Pelikan, Hannover, Germany) were placed into the access cavities and the training blocks were stored for 48 hrs at room temperature in a humidified

atmosphere. To make sure that the dye was not discoloured by the materials under investigation (Souza *et al*. 2009), drops of Royal Blue ink was placed on these. No discoloration was noted. Leakage was determined as length of penetrated ink into the simulated root canal. The length of leaked dye was given in % of the overall length of filled templates.

Data distribution related to immediate dye leakage was skewed and therefore compared using non-parametric statistics: Kruskal-Wallis anlaysis of variance was applied followed by Mann-Whitney U test for individual comparisons. Multiple testing was corrected for according to Bonferroni's method. The alpha-type error was set at 0.05.

Results

BG nanoparticles prepared by flame spray synthesis have been characterized and described in the literature (Brunner *et al.* 2006, Waltimo *et al.* 2007, Gubler *et al.* 2008, Misra *et al.* 2008). For this reason a thorough study on the BG particles was not performed. PI/30 wt% BG composite specimens showed a rough surface without a nanostructured topography (Fig. 2a) whilst PCL/30 wt% BG counterparts revealed parts with a homogenous dispersion of BG nanoparticles and parts with mere polymer in between (Fig. 2d). The contact angle, which is an indicator for hydrophilicity, did not change for PI specimens whilst for PCL samples a decreasing contact angle from 80° to 54° was observed when adding BG from 0 to 30 wt% (Table 1).

Immersion of the composite specimens in SBF revealed a tremendous surface change. After 7 days in SBF small apparent hydroxyapatite crystals (about 200 nm) covered the

surface of PI composites with 30 wt% BG (Fig. 2b). After 28 days the surface was completely covered and hydroxyapatite grew to micron-sized crystals. PCL/BG composites showed slightly less apatite growth than PI/BG counterparts. After 7 days, tiny apparent apatite structures were covering the surface whilst on day 28 the surface was covered completely (Fig. 2e, f). However, as opposed to the mature apatite structures obtained with PI/30 wt% BG, the typical structure of growing apatite was still visible on PCL/30 wt% BG specimens. In contrast to the experimental materials, commercial gutta-percha and Resilon showed predominantly micron-sized and sharp-edged particles in the polymeric matrix. After 4 weeks *in vitro* bioactivity test, SEM images indicated a comparatively smoother surface without precipitates (Fig. 3). For unfilled polymers and commercial materials no change of the XRD pattern was observed after the specimens had been immersed in SBF for 28 days. For PI/30 wt% BG and PCL/30 wt% BG peaks consistent with hydroxyapatite were discernible after 28 days (Fig. 4).

The mass loss of the composite blocks revealed different results for the two systems under investigation. PI specimens revealed a mean mass loss of up to 8%. Whilst the mass loss increased for higher BG content, it did not increase over time (Fig. 5a). PCL blocks had a mass loss of up to 18% for the specimens containing 30 wt% BG after 28 days in SBF. The mass loss increased for an increasing BG content, but it only rose for samples with 30 wt% BG over time in SBF. No mass change was detected with the commercial gutta-percha samples. Resilon specimens showed a minor mass loss (Fig. 5b).

Dye leakage in filled simulated root canals revealed that the unfilled polymers and the gutta-percha material under investigation allowed dye penetration along the root filling to

simulated canal wall interface to a statistically similar extent ($P > 0.05$, Fig. 6). Incorporation of 30 wt% BG into either of the polymers under investigation prevented immediate dye leakage completely. Resilon did not allow any leakage under the current conditions either. Immediate leakage differed at a statistically significant level ($P < 0.05$) between the BG-filled polymers and Resilon compared to unfilled PI/PCL and the gutta-percha material under investigation.

Discussion

In this study two composite systems using polyisoprene (PI) or polycaprolactone (PCL) in combination with bioactive glass 45S5 (BG) nanoparticles were developed. Both systems had high *in vitro* bioactivity and good initial sealing ability.

BG allocation in PI revealed a different dispersion pattern compared to that in PCL (Fig. 2a, d). In PI few areas were identified with nanoparticle dispersion. Particles were dispersed more homogeneously in PCL. In PI, the particles were either agglomerated on the surface or embedded under the surface (Mohn *et al.* 2010). The latter possibility was substantiated by the contact angle measurements (Table 1). PI samples did not show any change in contact angle, which supports the assumption that the particles were immersed under the surface. In contrast, the contact angle of PCL composites decreased with increasing BG content, suggesting faster liquid spread over the surface and a better wettability. This is in agreement with the dispersion of BG nanoparticles at the surface, as was observed using SEM. The minor increase from 20 to 30 wt% could be attributed to a partial separation of the particles and the polymer (Misra *et al.* 2008). Gutta-percha had

the same contact angle as the experimental PI composites. The water contact angle on Resilon was close to that of the PCL/10 wt% BG composite.

Although BG nanoparticles appeared to be underneath the surface of the PI composites, these materials showed cauliflower-shaped hydroxyapatite crystals on their surface after 7 days in SBF (Fig. 2b). The crystals were larger and more spherical than those growing on PCL composites (Fig. 2e). The faster apparent hydroxyapatite growth on PI samples was also corroborated by SEM images after 28 days. The surface of PI composites was covered with a layer of mature apatite crystals (Fig. 2c) whilst on PCL counterparts the corresponding structures appeared to be still growing (Fig. 2f). Hydroxyapatite apposition was also confirmed by XRD pattern after 28 days in SBF. For both polymer systems (PI and PCL) clear and broad hydroxyapatite reflections in the patterns were observed (Fig. 4). The broad signal reflected the nanometric size of hydroxyapatite crystals.

In contrast to the BG-containing PI and PCL materials, commercially available samples contained micron-sized particles (Fig. 3a, c). After immersion in SBF both commercial materials revealed a smoother surface (Fig. 3b, d) microscopically. However, distinct XRD patterns for both materials were observed, which did not differ from those observed with the untreated specimens (Fig. 4). Gutta-percha had sharp peaks for zinc oxide, a major content of commercial gutta-percha, and barium sulphate, which is added as a radiopacifier. In Resilon bismuth oxychlorid (radiopacifier) could be identified before and after immersion in SBF (Tay *et al.* 2005). According to the manufacturers material safety data sheet, additional fillers like barium sulphate, silica or barium-borosilicate glasses should be incorporated in the polymer matrix, but could not be identified using XRD.

The mass loss of the experimental composites (Fig. 5) did not only suggest degradation of the polymer matrix but also inorganic species leaking out of the composite. Both polymer systems showed a mass loss with increasing BG content. PCL with 30 wt% BG showed also a mass loss for prolonged immersion time. The PCL system exhibited double the mass loss compared to PI composites. SEM images of PCL composites (Fig. 2e, f) showed a more porous structure than PI/BG counterparts. It may thus be speculated that a higher water uptake was facilitated by the more porous structure of PCL/BG systems. This porous structure could increase leakage of BG components out of the polymer matrix, leading to a larger mass loss. However, for unfilled PI and PCL hardly any mass change could be detected. PI is a non-biodegradable polymer, whilst PCL is a biopolymer that undergoes slow degradation in wet environments (Pitt *et al.* 1981). Although the pure PCL had nearly no mass change it cannot be excluded that pore formation and the alkaline conditions created by the BG content had an influence on matrix degradation in PCL/BG composites. The inorganic content of composite specimens was checked blindedly using thermogravimetrical analysis. As prepared samples revealed that the mass of inorganic content was correlated to the amount of BG added. However, PCL/30 wt% BG composite exhibited different amounts of inorganic content at various time points during the 28 days of immersion in SBF. The inorganic content decreased from 30 to 22 wt% during the initial 14 days. After 28 days, however, PCL/30 wt% BG specimens showed an inorganic content of 32 wt%. Taking into account that BG contributed substantially to the mass loss by leaching out from the specimens, this increase of inorganic substance suggests that the precipitation of hydroxyapatite from the surrounding liquid replenished inorganic components. Therefore, ion leaching out of

the composite is probably responsible for the mass loss (Borbely *et al.* 2008) whilst hydroxyapatite precipitation can, at least partially, counter-balance this effect.

Dye leakage in root canal templates suggested a lower primary sealing ability of gutta-percha (Fig. 6) in comparison to Resilon under current conditions. This could be due to a better adaptation of the PCL-based Resilon to the epoxy resin of the simulated root canal wall. Alternatively, the different fillers contained in commercial gutta-percha and Resilon could be responsible for this observation. However, it must be noted that not all commercially available gutte-percha brands allow immediate dye leakage under the current conditions (data not shown). Furthermore, it must be cautioned in this context that the epoxy resin models used in this study have little in common with root canals in natural teeth. The pure PI polymer also allowed dye leakage. In contrast, pure PCL leaked substantially more than the filled commercial material (Resilon). Interestingly, adding 30 wt% of nanosized BG to PI and PCL prevented dye penetration completely. Similar findings have been shown most recently for PCL and a phosphate-based glass (Alani *et al.* 2009). In the latter study, ion precipitation was held responsible for the adaptation of the material to the canal wall. However, the current set-up tested immediate leakage, which has been a problem with aqueous BG suspensions, as precipitate formation takes time (Zehnder *et al.* 2007). A possible explanation for the improved prevention of dye leakage by the PI/BG and PCL/BG composites compared to pure polymers could be the fast absorption of liquid into BG, which may cause particle expansion and thus enhance marginal adaptation of the polymer matrix to the simulated canal wall.

The current study showed promising results for the bioactive composite materials under investigation. Replacement of the inert fillers in PI- and PCL-based root filling materials by bioactive particles could make the use of a sealer unnecessary in the near future. Further investigations should test the adaptation of bioactive composite root filling materials to canal walls of human teeth under simulated clinical conditions. Furthermore, the incorporation of radiopacifiers into these systems and their tissue compatibility should be evaluated before they can finally be applied and evaluated clinically.

Conclusion

Incorporation of bioactive glass fillers into polyisoprene and polycaprolactone made the resulting composite materials bioactive and improved their immediate sealing ability.

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Captions

Figure 1

Photographic images of standardized dental training blocks with plugged lateral canals and without a root canal filling (left), filled with PI/30 wt% BG (middle), and filled with PCL/30 wt% BG (right).

Figure 2

SEM images of polyisoprene/30 wt% BG (a-c) and polycaprolactone/30 wt% BG (d-f) composite samples before and after immersion in SBF. PI/30 wt% BG as prepared (a), after 7 days (b) and 28 days (c) immersion in SBF with apparent hydroxyapatite covering the surface. PCL/30 wt% BG as prepared (d) showed nanoparticle dispersion and after 7 days in SBF (e) revealed apparent hydroxyapatite growth on the surface. 28 days SBF (f) immersion resulted in apparent hydroxyapatite coverage.

Figure 3

SEM micrographs of commercial materials: Obtura gutta-percha (a, b) and Resilon (c, d). The as-prepared commercial gutta-percha material (a) showed a rough surface, which was smoothened after immersion in SBF for 28 days (b). Resilon sample as prepared (c) showed large and irregular fillers. After 28 days in SBF (d) the surface was smoothened.

Figure 4

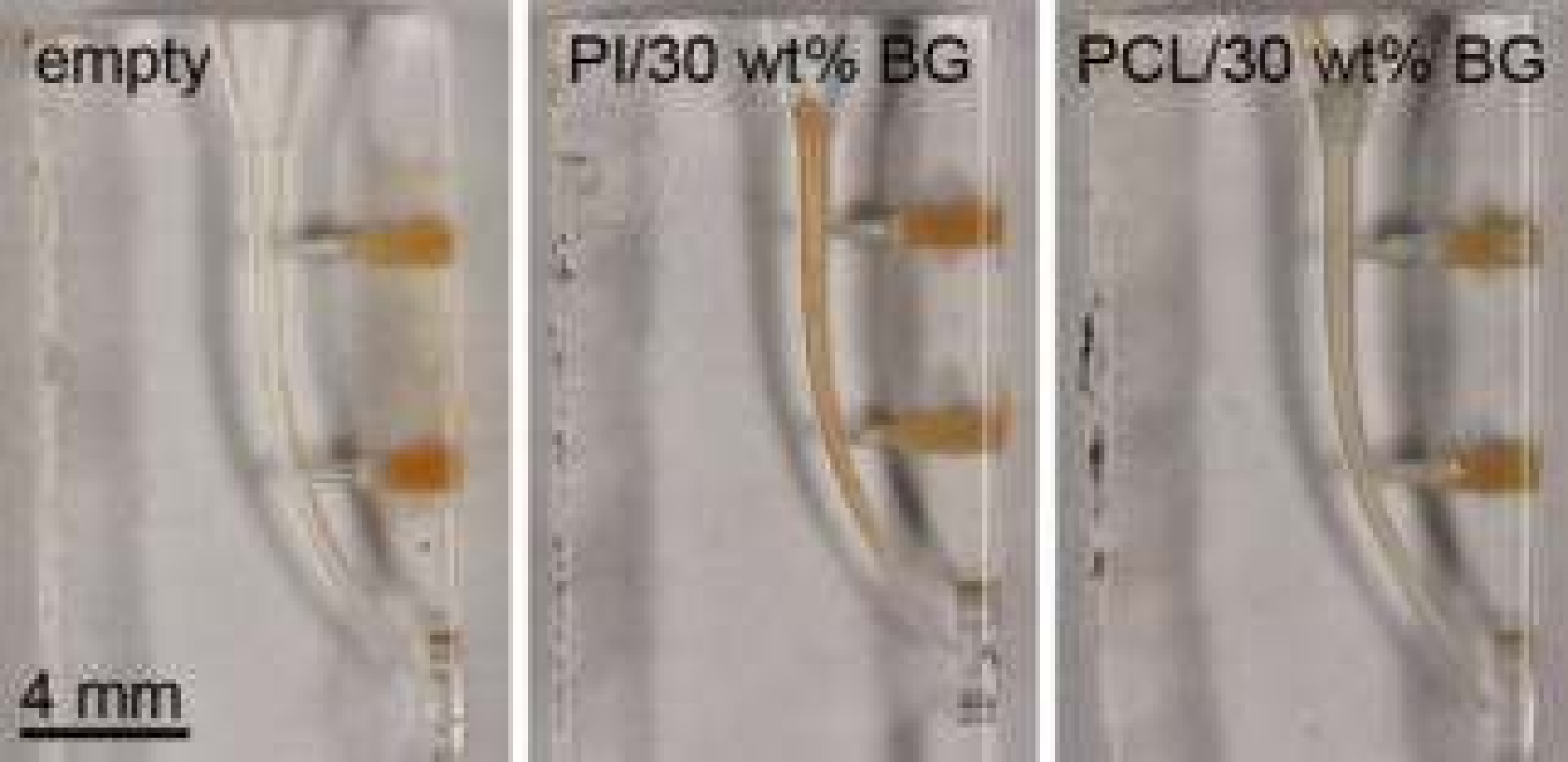
X-ray diffraction pattern of specimens with PI (a) and PCL (b) as matrix. Obtura gutta-percha samples (a) before and after SBF immersion showing unaltered pattern whilst hydroxyapatite appeared with the PI/30 wt% BG sample after 28 days in SBF. PCL as matrix material (b) resulted also in hydroxyapatite growth (the intensity of the XRD pattern was multiplied with a factor of 2 and 5 for PI/30 wt% BG and PCL/30 wt% BG, respectively).

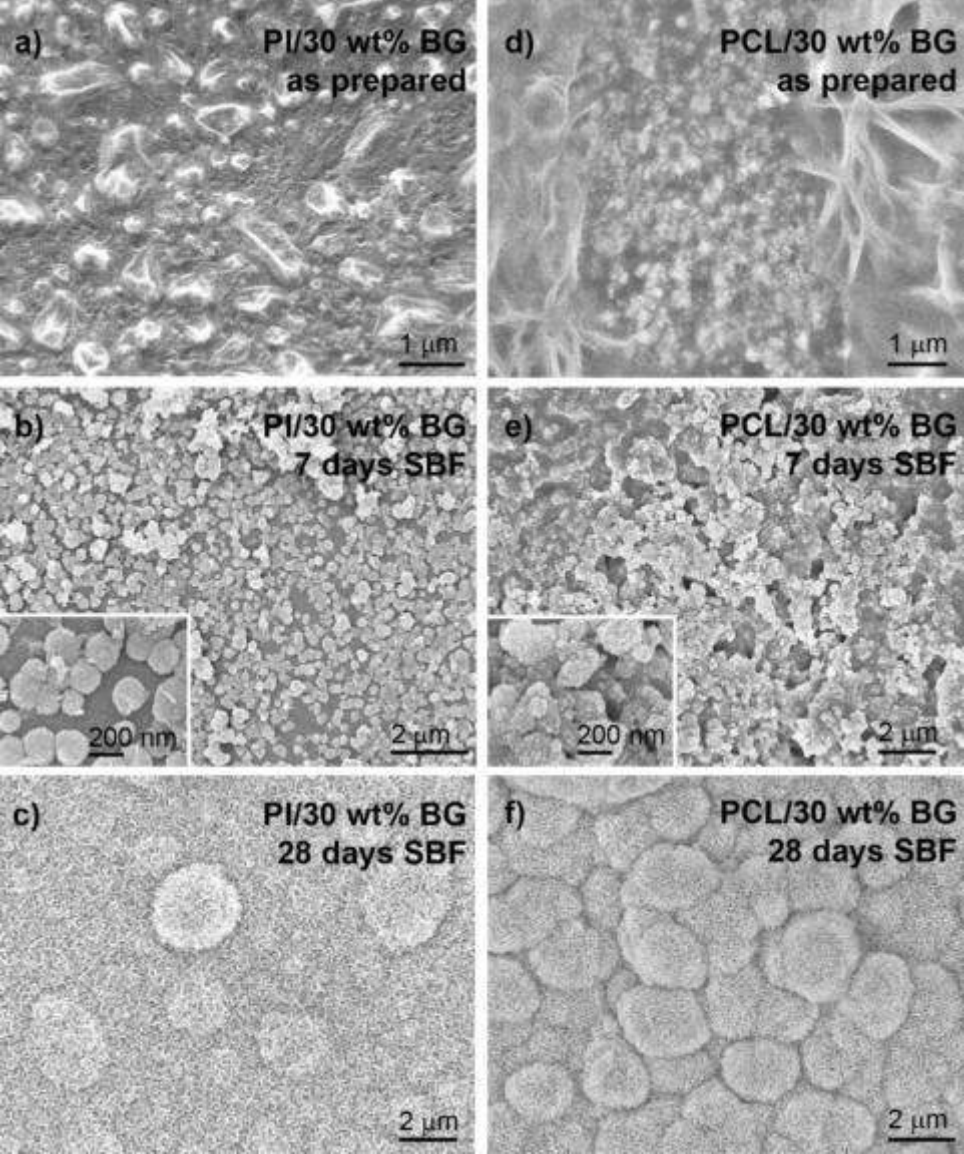
Figure 5

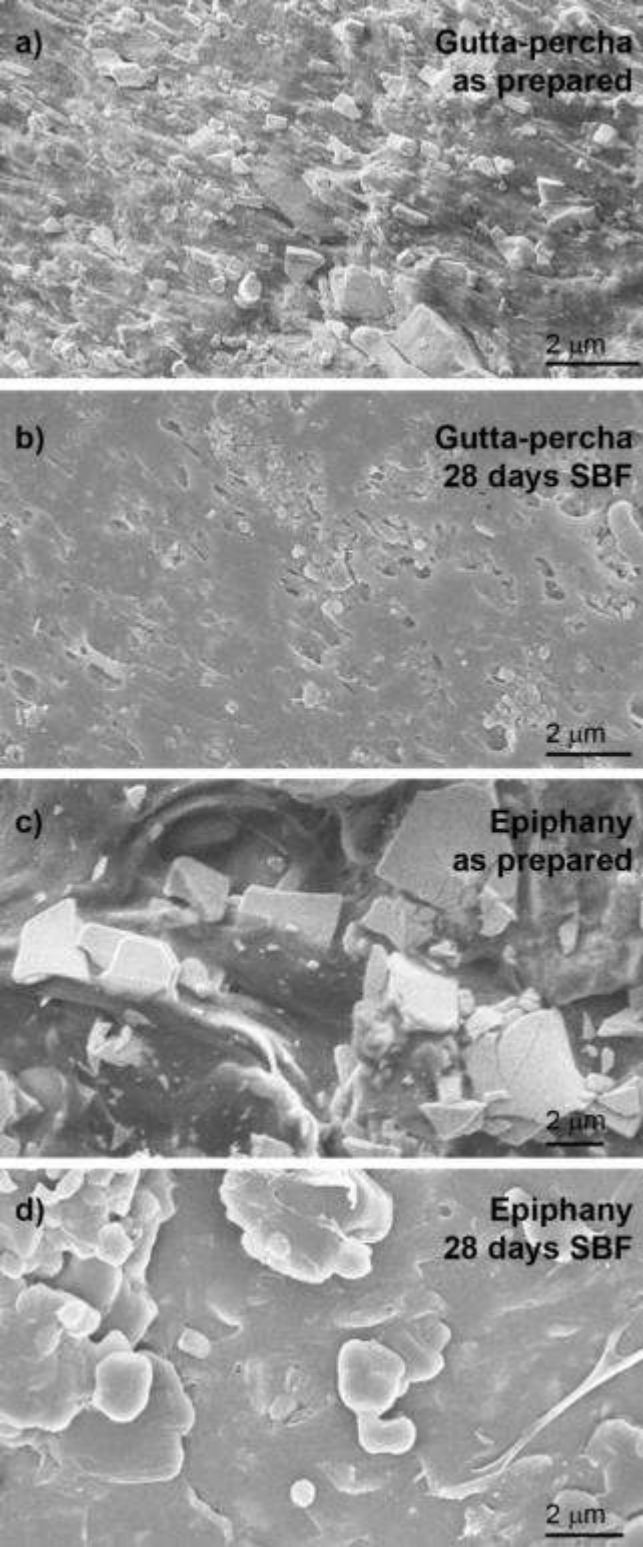
Mass loss of PI samples (a) for different bioactive glass content and different time periods (* only two specimens tested). PCL samples (b) revealed an elevated mass loss for increased BG contents. 30 wt% BG content resulted in increased mass loss for longer immersion in SBF. Resilon (RES) samples showed a minor mass loss.

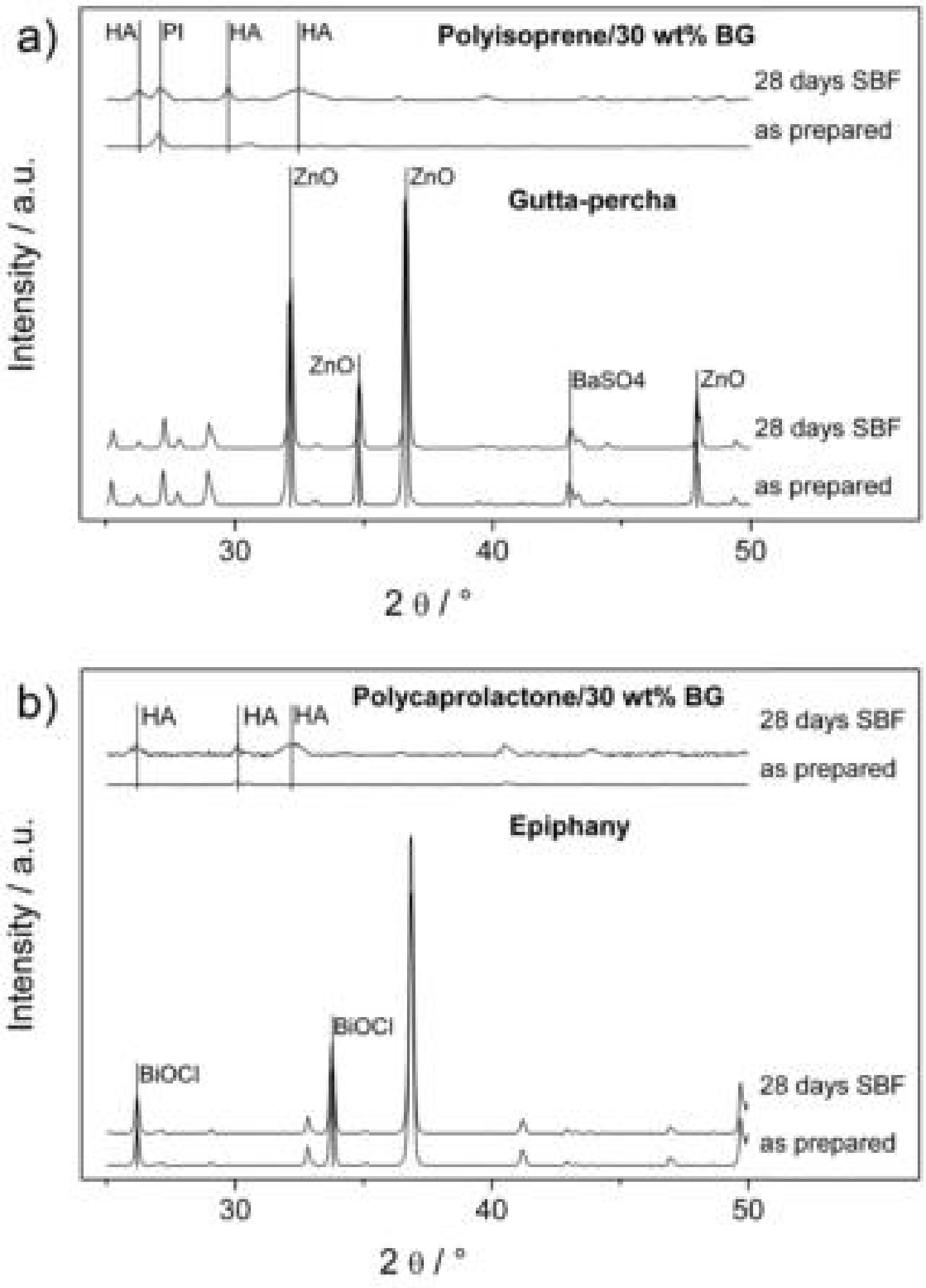
Figure 6

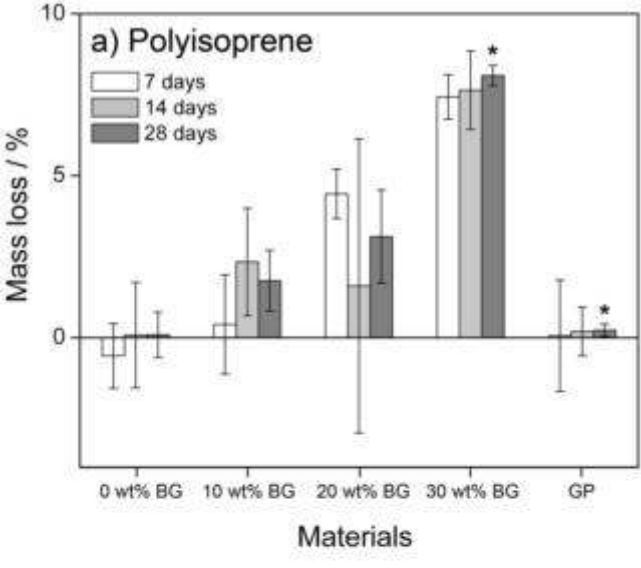
Dot plot (a) indicating dye leakage as % of total canal length in simulated root canals obtained with the different materials under investigation (N = 6; identical superscript capital letters indicate that data sets were statistically similar). Photographic images of Obtura gutta-percha (b) and PI/30 wt% BG (c) after 2 days of exposure to the dye. RES: Resilon.

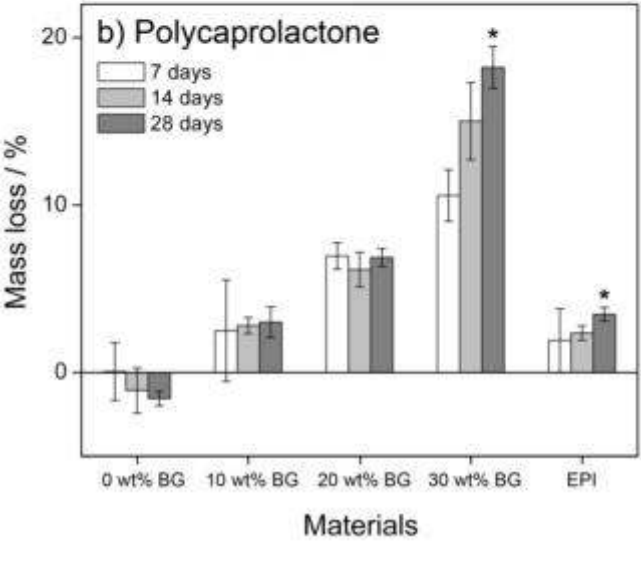

empty
PI/30 wt% BG
PCL/30 wt% BG
4 mm

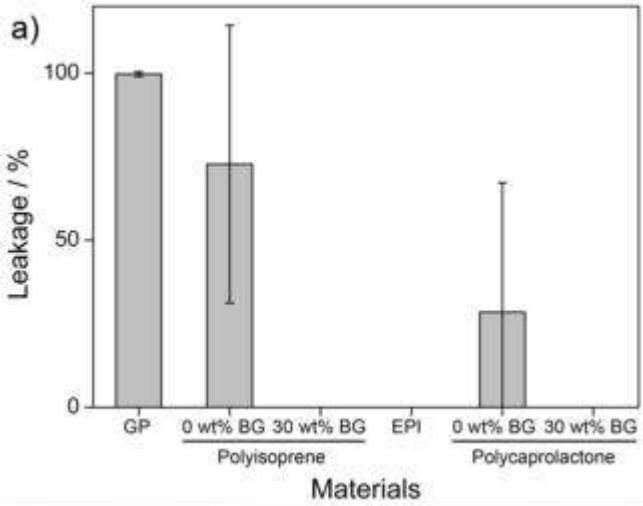

a)
PI/30 wt% BG
as prepared
1 μm
d)
PCL/30 wt% BG
as prepared
1 μm
b)
PI/30 wt% BG
7 days SBF
200 nm
2 μm
e)
PCL/30 wt% BG
7 days SBF
200 nm
2 μm
c)
PI/30 wt% BG
28 days SBF
2 μm
f)
PCL/30 wt% BG
28 days SBF
2 μm


a)
Gutta-percha
as prepared
2 µm
b)
Gutta-percha
28 days SBF
2 µm
c)
Epiphany
as prepared
2 µm
d)
Epiphany
28 days SBF
2 µm


a)
HA
PI
HA
HA
Polyisoprene/30 wt% BG
28 days SBF
as prepared
ZnO
ZnO
Gutta-percha
ZnO
BaSO4
ZnO
28 days SBF
as prepared
Intensity / a.u.
30
40
50
2 θ / °
b)
Polycaprolactone/30 wt% BG
HA
HA
HA
28 days SBF
as prepared
Epiphany
BiOCl
BiOCl
28 days SBF
as prepared
Intensity / a.u.
30
40
50
2 θ / °


a) Polyisoprene
7 days
14 days
28 days
Mass loss / %
10
5
0
*
*
0 wt% BG
10 wt% BG
20 wt% BG
30 wt% BG
GP
Materials


b) Polycaprolactone
7 days
14 days
28 days
Mass loss / %
20
10
0
*
*
0 wt% BG
10 wt% BG
20 wt% BG
30 wt% BG
EPI
Materials


a)
100
50
0
Leakage / %
GP
0 wt% BG
30 wt% BG
EPI
0 wt% BG
30 wt% BG
Polyisoprene
Polycaprolactone
Materials


b)
4 mm


c)