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Flexural Properties of Glass Fibre Reinforced Composite with Partially Biodegradable Polymer Matrix

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Summary: The aim of this study was to evaluate flexural properties of a partially biodegradable glass fibre reinforced composite after water immersion and dehydration. In addition water sorption and solubility was determined. E-glass fibres were preimpregnated with a biodegradable biopolymer of poly(hydroxyproline) amide (PA). The preimpregnated fibres were then further-impregnated with Bis-GMA–TEGDMA-resin and light polymerized ($n = 6$). There was also specimen made of plain polymer and FRC without PA. After water immersion and/or dehydration, the specimens were tested by the three-point bending test. The flexural strength and Young's modulus was increased in most cases after water immersion and dehydration except for PA containing specimens. The water sorption was <50 μg/mm^3 for all studied specimens and solubility was 20 μg/mm^3 for specimens without PA and 35 μg/mm^3 for specimens with PA.

Keywords: biopolymers; composites; dental polymers; mechanical properties

Introduction

A fibre-reinforced composites (FRC) have recently been evaluated for dental and surgical bone applications to replace metals because of their better biomechanics (stiffness and strength of the composite) with a bone compared to the metal. Strength and stiffness are important mechanical properties in load-bearing applications, e.g. in long-bone repairs or in other critical size defects caused by e.g. a tumor or a trauma. A polymer (e.g. poly(methyl methacrylate), PMMA) as such has not enough a mechanical strength for load-bearing applications, and thus there have been attempts to reinforce polymers with whiskers or short fibres.[1,2] By using continuous fibres to reinforce polymers, even more durable composites can be achieved.[3,4] FRC have already successfully been used in several dental applications such as removable prosthesis,[5] fixed partial dentures[6,7] and root canal posts.[8] In bone surgery, FRCs has been proposed, and some of them have also been used, for e.g. fixation plates[9–11] or even as hip prosthesis.[12] Using continuous unidirectional glass fibre-reinforced PMMA, the flexural strength and the modulus of elasticity are close to[13] that of human femur.[14] *In vitro* tests with a novel partially biodegradable FRC showed even higher values for the strength and the stiffness.[15] With the amount and the position or orientation of the fibre reinforcement, the mechanical properties could be tailored to the suitable level for the particular applications.[16–18]

In dental and bone applications, the implant is contact with a body fluid (saliva, interstitial fluid or blood); thus, water is diffused into the polymeric device or cement. Water, as well as some other small

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molecules, can penetrate into the polymer matrix of the composite and act as a plasticizer which decrease the mechanical properties of the composite.[19–22] However, the decrease of mechanical properties is shown to be reversible. If the composite has been dehydrated after water storage, the mechanical properties recover.[16] In addition to the penetration of the water molecule, when the composite is exposed to the water, residual monomers and other residual substances (which can also act as plasticizers) leach out from the composite[23,24] thus making the composite higher in strength and stiffness after dehydration. Obviously, this phenomenon has limited clinical impact but it is relevant from materials science perspective. The amount of the penetrated water into the composite can be evaluated by the aid of a water sorption and solubility tests. The water sorption and solubility of the polymer matrix depend on the hydrophilicity of the matrix.[25] Fibre reinforcement lowers the water sorption and solubility because of the less amount of the water absorbable polymer in FRC.[25] However, if the fibres of the FRC are poorly impregnated with resin, water sorption of the FRC can even be higher than for plain polymer.[26]

Attempts have been made to develop FRC having partially degradable polymer matrix, which could allow formation of pores for bone to grow in and attach mechanically to the implant.[27] In aqueous environment, it has been found that open canals can form between the fibre and polymer matrix of the partially biodegradable FRC, it might assume that these open canals can diminish the mechanical properties of the FRC or influence on the water sorption or solubility of the FRC. The aim of the study was to determine the effect of the water immersion and dehydration to the flexural properties of the FRC with partially biodegradable polymer matrix. In addition, water sorption and solubility was determined.

Materials and Methods

The bifunctional monomer resin system was prepared, as described earlier, by mixing Bis-GMA and TEGDMA in a ratio of 70:30 wt%/wt%.[15] Dimethyl amino ethyl methacrylate (DMAEMA) (0.35 wt %) was used as a catalyst and camphorquinone (0.35 wt %) was used as a light polymerization initiator.

Three different test groups (Table 1, $n = 6$) were investigated in this study. Continuous unidirectional E-glass fibres (containing about 4000 fibres, $\emptyset = 14$ μm) (composition: SiO_2 55 wt%, CaO 22 wt%, Al_2O_3 15 wt%, B_2O_3 6 wt%, MgO 0.5 wt% and Fe + Na + K less than 1.0 wt%), which were silanized (process R332, Ahlström, Karhula, Finland), were preimpregnated with an experimental linear biopolymer of poly(4-hydroxy-L-proline) amide[28] (PA, $M_{vis} = 2200$ g/mol) in TFE solution(50 mg/ml). After evaporation of the solvent, the bundle of fibres was further impregnated with the Bis-GMA- TEGDMA resin for 24 hours. Preimpregnated fibres were placed parallel to each other into stainless steel moulds (size: $2 \times 2 \times 25$ mm^3) with an excess of the resin system. The test specimens were initially polymerized with an Optilux 501 (SDS, Kerr/Demetron, Danbury, USA) light-polymerization unit ($\lambda =$ 480 nm, light intensity ca 600 mW/cm^2), for 40 seconds on both sides. Subsequently, the test specimens were post-cured with a light-curing device (LicuLite, Dentsply DeTrey GmbH, Dreieich, Germany), for 15 minutes. After polymerization, the specimens

Table 1.
Description and classification of used test groups.

Group	Description
BT	Bis-GMA/TEGDMA
BTE	Bis-GMA/TEGDMA + E-glass fibres
BTES	Bis-GMA/TEGDMA + E-glass fibres with PA preimpregnation

Table 2.
The description of the treatment of the studied test specimens.

Treatment	Description
Dry[15]	7 days in RT in a desiccator
Water7	7 days in water at +37 °C and dehydrated at least for 3 days at +40 °C
Water30	30 days in water at +37 °C and dehydrated 26 days to constant weight at +40 °C
In water	14 days in water at +37 °C

were treated according to the Table 2 before flexural tests.

Three-point bending test (span 20 mm) are used to measure the flexural strength and Young's modulus of the specimens. Tests were done according to the ISO 10477:92 standard using a Lloyd Instruments LRX Material testing machine (Lloyd Instruments Ltd., Fareham, England), at a cross-head speed of 1 mm/min, and the stress-strain curves were drawn with a PC program (Nexygen, Lloyd Instruments Ltd., Fareham, England). Test specimens were tested at RT (24 ± 2) °C in humidity of (31 ± 7) % except "in water" specimen, which were tested in the water at +37 °C. The ultimate flexural strength (FS/MPa) was calculated from the formula:

$$FS = 3Fl/2bh^2$$

where F is the applied load (N) at the highest point of the load-deflection curve, l is the span length (20 mm), b is the width (2.0 ± 0.1) mm and h is the height (2.0 ± 0.1) mm of the test specimen. Young's modulus (YM/GPa) of the test specimens was calculated from the following formula:

$$YM = Fl^3/4bh^3d$$

where d is the deflection (mm) corresponding to the load F, at a point on the straight-line portion of the trace.

A quantity of fibres in the test specimens was determined by combustion of the polymer matrix of the test specimens for one hour at 700 °C. The test specimens were weighed before and after combustion. The fibre content of the test specimens were calculated by the following formula:

$$m_f\% = (m_f/m_t)^*100\%$$

where m_f % is the mass percentage of fibre, m_f is the mass of fibre after combustion and m_t is the mass of test specimen. Volume fraction (V/vol %) of the fibres was calculated by using the following formula [29]:

$$V = (W_f/r_f)/(W_f/r_f + W_r/r_r)$$

where W_f is the weight proportion of reinforcement, r_f is the density of reinforcement (2.54 g/cm^3), W_r is the weight proportion of resin and r_r is density of resin (1.19 g/cm^3).

For water sorption and solubility test, the test specimens were first immersed in ion-exchanged water at +37 °C for 30 days and then dehydrated at +40 °C for 26 days to the constant weight. The dry weight (m_1) of the specimens was measured with an accuracy of 0.1 mg and the dimensions of the specimens (b = breadth, h = height, l = length) were determined with an electronic digital calliper (an accuracy ±0.03 mm) for three different points for all sides in order to determine the volume of the specimens (V/mm^3). After immersion in water, the specimens were blotted to remove surface water and weighed (m_2) and dehydrated to constant weight (m_3). Water sorption (W_{sp}/μgmm^{-3}) and solubility (W_{sl}/μgmm^{-3}) was calculated by the following formulas:

$$W_{sp} = (m_2 - m_3)/V \quad \text{and}$$

$$W_{sl} = (m_1 - m_3)/V$$

Results

The flexural strength in the BT group was slightly increased after water immersion and dehydration from 81 MPa to the about 100 MPa (Figure 1A). Minor increase was also found for the BTE group (from 805 to 838 MPa). If the specimens were not

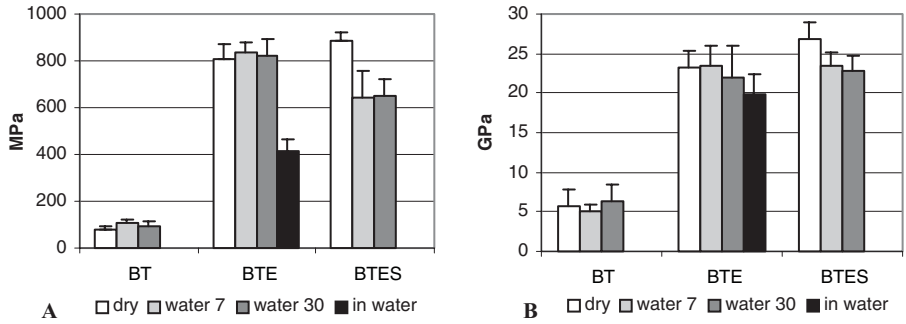

Figure 1.
The ultimate flexural strength (A) and Young's modulus (B) of the test specimens before and after water treatment. A vertical line represents standard deviations.

dehydrated, reduction in strength was ca. 50% (411 MPa). In the group BTES, the flexural strength decreased after water immersion and dehydration (from 888 to about 650 MPa).

The Young's modulus of the specimen BT was slightly increased after 30 days of water immersion and dehydration from the 5.7 to 6.2 GPa (Figure 1B). In BTE group, there was minor decrease compared to the dry group except for the specimen without dehydration. When group BTES was immersed in water and dehydrated, the Young's modulus was decreased from 27 GPa to 23 GPa.

The quantity of glass fibres was 0 vol% (0 wt%) in BT group, 40.8 vol% (59.6 wt %) in BTE group and 34.1 vol% (52.6 wt%) in BTES group.

Water sorption and solubility values are shown in the Table 3.

Discussion

This study investigated the flexural properties of FRC with a partially biodegradable matrix after water immersion and dehydration, and determined water sorption and solubility of the composite. The flexural strength and Young's modulus of elasticity of the FRC was highest in the dry group BTES, which was found in earlier study.[15] After water immersion and dehydration, the mechanical properties of BTES decreased because of the degradation of PA and thus the formation of pores between the fibres and the polymer matrix. After water immersion and dehydration, the highest value of flexural strength was in the BTE group, which can be explained by leached residual monomers during water immersion, which in turn, made the composite stiffer after the specimen had been dehydrated. However, as can be seen, BTE without dehydration showed much lower strength than other BTE subgroups. This has also been found in another study.[16] The penetrated water molecules in FRC reduced considerably the strength of the composite. This can be caused by the poor degree impregnation of the fibres with the resin during fabrication the specimens.

In general, materials with lower filler or fibre content, i.e. higher polymer content had higher water sorption[30] as also was

Table 3.
The water sorption and water solubility values of the specimens (±SD).

Group	Water sorption/$\mu g mm^{-3}$	Water solubility/$\mu g mm^{-3}$
BT	48.4 ± 1.9	22.0 ± 12.2
BTE	41.8 ± 7.4	20.4 ± 6.4
BTES	–	35.7 ± 7.7

found in this study when compared the specimens of BT and BTE groups. There was also relation between the mechanical properties and the water sorption and solubility: the higher the water sorption and solubility were, the lower were the mechanical properties.[31] For dental restorative resins (typically dimethacrylate based), ISO standards (4049) give limit values for the water sorption of less 50 $\mu g/mm^3$ and for solubility less than 5 $\mu g/mm^3$. In this study, the water sorption was less than 50 $\mu g/mm^3$ but the solubility was higher (> 20 $\mu g/mm^3$) in all specimens. For Bis-GMA/TEGDMA (50/50 wt%) resin, it has been determined values of 28 $\mu g/mm^3$ for water sorption and 2.4 $\mu g/mm^3$ for solubility[32] whereas for the resin composition 70/30 wt%, values are 35 $\mu g/mm^3$ for water sorption and −3.11 $\mu g/mm^3$ for solubility.[33] It could be possible, that high water sorption and solubility values in this study was because of low monomer conversion of the polymer matrix, which left higher quantities of residual monomers inside the composite enhancing leaching of monomers and diffusion of water in to the composite. Another technical explanation could be that there were air bubbles in the polymer matrix, which were not detected by visual inspection. In the case of the BTES group, the solubility was high, likely because of the hydrophilicity and the dissolution of the biodegradable PA leaving open pores to the composite.

The clinical applications of the FRC material with multiphase biopolymer matrix could be variety of bone surgery applications. The present findings suggest that the strength of FRC as material, even after water immersion, can be high enough to fulfil the strength requirement for some bone applications. It should be noted, that the strength of the possible implant device is not only related to the properties of the material, but also to the dimensioning of the device. However, further *in vivo* studies are needed to show the behaviour of the FRC with a multiphase biopolymer matrix, in an environment of the body.

Conclusions

The flexural properties of FRC with partially biodegradable polymer matrix were decreased after water immersion. Dehydration of the FRC after water immersion showed somewhat recovered mechanical properties.

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