Release of fluoride from glass fiber-reinforced composite with multiphase polymer matrix

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This study investigated the suitability of a fluoride containing monomer resin system for use as a copolymer of dental fiber-reinforced composite (FRC) materials. The purpose of the study was to measure the release of fluoride from the test materials. The monomer resin system was either light-polymerized, or light-polymerized and post-cured with heat at 130°C. The release of fluoride from FRC test specimens during 30 day storage periods was compared to the release of fluoride from unreinforced test specimens ($n = 5$). The fluoride release into distilled water was determined with an ionanalyzator. During the first week of water storage, the fluoride release was 0.31 wt % for the unreinforced specimens and 0.13 wt % for reinforced specimens. The post-curing had no influence on the fluoride release values. The results of this study suggest that fiber inclusion reduces fluoride release of reinforced specimens compared to unreinforced specimens because the amount of polymer was smaller in reinforced specimens. The results of this study showed that the fluoride containing monomer system could be incorporated into the polymer matrix of fiber-reinforced composites.

1. Introduction

Glass fiber-reinforced composites (FRC) have been tested in different applications in dentistry [1–3]. They are already being used clinically as reinforcement of removable prostheses, fixed partial dentures and periodontal splints. The known ability of the fluoride ion to prevent caries when prevention in an oral environment is in small concentrations, has led to the development of fluoride-containing dental materials. There are many reports on the long-term release of fluoride from fluoride-containing dental materials, such as glass-polyalkenoate (glass ionomer) cements and fluoride–containing bonding agents for restorative composites [4–6]. To our knowledge, there are no published studies regarding the use of fluoride-containing monomer resin systems with FRC materials. The aim of this study was to test the release of fluoride from a fluoride-containing monomer resin system used as a co-monomer of polymer preimpregnated FRC material.

2. Materials and methods

Prime&Bond 2.1 (PB, DeTrey Dentsply, Konstanz, Germany) is a light-polymerizable monomer resin system, which has an application as dentin-enamel bonding agent for restorative composite resins. The PB monomer resin system contains dimethacry late monomers, dipentaerythritol penta acrylate monophosphate (PENTA) monomers, photo initiators, stabilizers, cetylamine hydrofluoride and 80 vol % acetone according to the manufacturer's information. Prior to using the PB monomer resin system as a co-monomer of preimpregnated FRC material (prepreg), the solvent acetone was evaporated from the resin at a temperature of 23 ± 1°C for five hours in a dark chamber. E-glass fibers (composition: SiO_2 55%, CaO 15%, Al_2O_3 15%, B_2O_3 6%, MgO 0.5%, Fe + Na + K1.0%) were used as unidirectional continuous fibers which were preimpregnated with porous polymethyl methacrylate (PMMA) (Stick®, Stick Tech Ltd, Turku, Finland) (Code: S) (Fig. 1a). Ten rhombic unreinforced and ten S-reinforced test specimen ($2 \times 2 \times 25$ mm) were made in a mold with polysiloxane axial walls and microscopic glass plates as bottom and coverage. Classification of test specimens is presented in Table I. Test specimens made from S-reinforcements which were wet with the PB monomer resin system were polymerized using a light curing unit (Visilux 2, Model 5520A, 3M, St. Paul, MN, USA) with a wave length of approximately 470 nm. The light exposure time was 2×40 s. Wetting of porous prepolymer matrix of the S-reinforcement with PB monomer resin system plasticized the prepolymer

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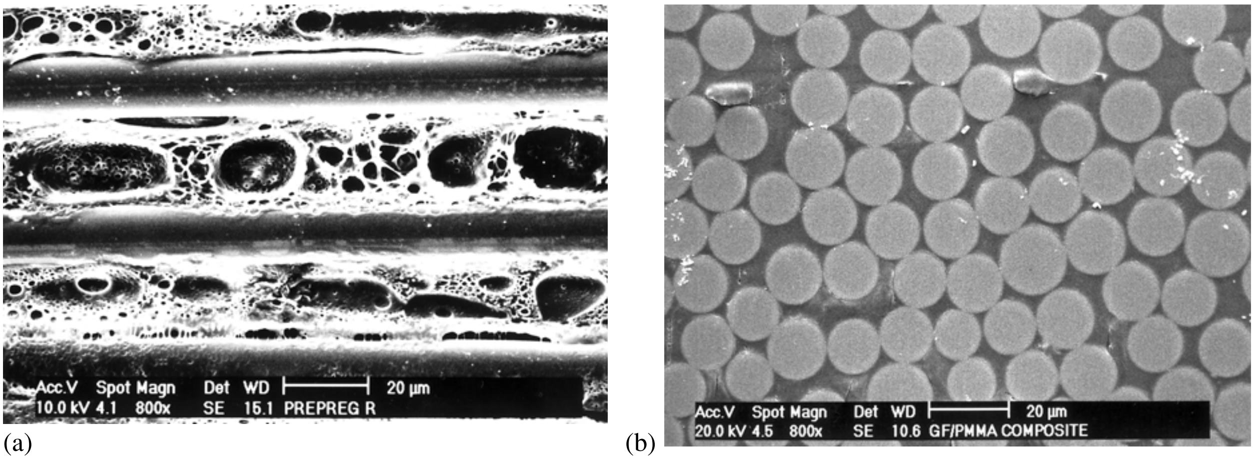

(a) (b)

Figure 1 Scanning electron micrograph of (a) longitudinal section of porous preimpregnation polymer of S-reinforcement and (b) cross-section of polymerized FRC material with multiphase polymer matrix. Original magnification was 800 ×, bar = 20 µm. (Reprinted with kindly permission of Mosby Company.

TABLE I Classification of the test specimens

Group	Fibers	Post-curing
1	No	No
2	No	Yes
3	Yes	No
4	Yes	Yes

matrix by dissolution and allowed fibers to be packed closely to each other after polymerization (Fig. 1 b) [7]. After light-polymerization, five S-reinforced test specimens and five unreinforced test specimens were post-cured with heat at 130 ± 5°C for 2 h. The post-curing temperature was selected according to the glass transition temperature (T_g) of dimethacrylate polymers which is approximately 130 °C [8]. After polymerization, the test specimens were put in a deionized water (aqua purif.) in test tubes and placed into a desiccator for storage at a temperature of 37 ± 1°C. The storage water was renewed after 7, 14 and 30 days. The fluoride concentration released into water as ppm was assessed by an iono-specific electrode and connected with an instrument for measurement (A 940 ionanalyzator, Orion Research Inc.) The results were also calculated as wt % from the original weight of the test specimens.

3. Results

Mean quantities of fluoride released in distilled water as wt % and as ppm are presented in Figs 2 and 3. The post-curing with heat had no influence on the fluoride release ($p = 0.929$, ANOVA), but fiber inclusion reduced fluoride release of each test group ($p < 0.001$, ANOVA). Mean quantities of fluoride released by each test group into water during the first week of storage were: 0.30 wt % (SD ± 0.05), (298.7 ppm SD ± 48.2) in unreinforced, not post-cured test group (1) 0.31 wt % (SD ± 0.02), (298.5 ppm SD ± 17.5) in unreinforced, post-cured test group (2) 0.12 wt % (SD ± 0.0008), (120.7 ppm ± SD7.5) in reinforced, not post-cured test group (3) and 0.13 wt % (SD ± 0.0007), (124.3 ppm SD ± 8.1) in reinforced, post-cured test group (4) During days 7 to 14 quantities of fluoride released were: 0.07 wt % (SD = 0.01), (68.9 ppm SD ± 11.6) in group 1, 0.06 wt % (SD ± 0.0005), (56.3 ppm SD ± 5.6) in group 2, 0.03 wt % (SD = 0.0003), (26.8 ppm SD ± 2.4) in group 3 and 0.03 wt % (SD ± 0.007), (29.9 ppm SD ± 6.8) in group 4. During days 14 to 30 the quantities of fluoride released were: 0.11 wt % (SD ± 0.01), (106.0 ppm SD ± 12.6) in group 1, 0.08 wt % (SD ± 0.05), (81.5 ppm SD ± 56.5) in group 2, 0.04 wt % (SD ± 0.0006), (38.9 ppm SD ± 6.4) in

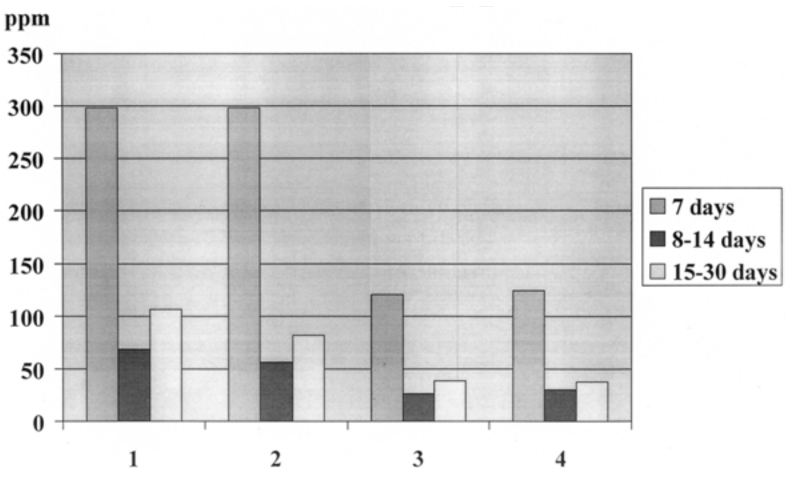

Figure 2 Mean quantity of released fluoride as ppm.

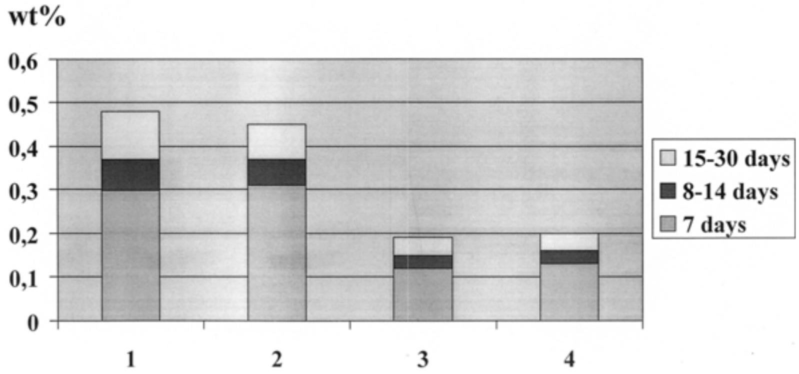

Figure 3 Mean quantity of release fluoride as weight percentage.

group and 0.04 wt % (SD ± 0.0007), (37.4 ppm SD ± 6.8) in group 4.

4. Discussion

The results of this study suggest that the fluoride-containing PB monomer system could be incorporated into the polymer matrix of dental FRC material and that the fluoride was released from the multiphase polymer matrix of the FRC material. The monomers of the PB resin system penetrated into the porous prepolymer matrix polyethyl methacrylate (PMMA) of the S-reinforcement and dissolved it during wetting of the prepreg. The dissolved macromolecules of PMMA (molecular weight 220 000) remained in the matrix of the polymerized matrix of the FRC and resulted in a multiphase polymer matrix for the FRC material. The quantity of released fluoride was lower from the test specimens with fiber-reinforcement compared to that of unreinforced test specimens. This was obviously due to a lower volume fraction of fluoride-releasing polymer matrix compared to that of unreinforced test specimens. Fiber volume fractions of FRCs in dental applications are relatively low, varying in applications such as removable prostheses from 5 to 25 vol % [9, 10] and being somewhat higher in other applications like fixed partial dentures [11]. The use of such low volume fractions of fibers in FRCs could be justified by using high quality FRC materials and accurate placing of FRC reinforcements in dental construction in terms of biomechanics of the masticatory system [1].

Post-curing of the polymer matrix of FRC did not influence the fluoride release of the FRC material. This could be explained by the ion radius of the fluoride ion (1.3Å [12] which allowed fluoride ions to diffuse through the spaces between polymer chains of the polymer matrix of the FRC even with a high degree of conversion of the polymer matrix after post-curing. The interchain spacing of amorphous polymers varies between 4.8 and 10 Å [13]. On the other hand, the post-curing of the dimethacrylate polymer has been shown to improve the physical properties of the FRC, which is desirable for the restoration of prosthetic dental materials. Consequently, the post-curing of polymer matrix of the FRC seems to be justified from these perspectives.

The caries preventative effect of fluoride is highest when low concentrations of free fluoride ions are constantly present in the oral environment. Even small amounts of fluoride released by a restoration may be beneficial from the clinical perspective and in theory contribute to the prevention of secondary caries [14, 15], even if such effects of fluoride-containing materials are difficult to show clinically [16, 17].

The results show that during the first 30 days the test specimens continued to release fluoride, even if the amount was highest during the first 7 days. The amounts of fluoride released by the test specimens is in line with results on fluoride-containing composites [18]. The test results combined with other results of the dental FRC developing project show that dental FRCs may well have applications also as restorative materials in dentistry.

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