

Long-term fluoride release from a glass ionomer cement, a compomer, and from experimental resin composites

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The aqueous phase of glass ionomer cements enables fluoride ions to diffuse and to be released from the material. The matrix of resin composites is much less hydrophilic, and fluoride incorporated in the material is only released in small amounts. It was the purpose of the present work to study the influence of resin matrix formulation on the fluoride release from experimental, fluoride-containing resin composites. The resin composites were based on methacrylate monomers and the adduct of maleic anhydride and HEMA (2-hydroxyethyl methacrylate). The resin composites contained 1 w% or 5 w% of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$. A glass ionomer cement and a compomer were used as controls. Five disks of each material were stored in distilled water at room temperature. By means of a fluoride sensitive electrode, the fluoride release from disk-shaped specimens was determined periodically over 3 years. The glass ionomer cement released the most fluoride ($154 \pm 4 \mu\text{g}/\text{cm}^2$ after 1 year and $248 \pm 7 \mu\text{g}/\text{cm}^2$ after 3 years). The compomer released relatively little fluoride during the 1st year ($30 \pm 1 \mu\text{g}/\text{cm}^2$), but after this time the rate of fluoride release became equal to that of the glass ionomer cement, resulting in a release of $122 \pm 8 \mu\text{g}/\text{cm}^2$ after 3 years. Regarding the resin composites, the fluoride release increased with the hydrophilicity and the acid character of the polymer matrix. The release, however, was significantly lower than that from the glass ionomer cement and the compomer and ranged from 1.2 ± 0.07 to $42 \pm 3.9 \mu\text{g}/\text{cm}^2$ at 1 year and from 2.3 ± 0.16 to $79 \pm 6 \mu\text{g}/\text{cm}^2$ at 3 years. □ *Acidic monomer; dental materials; hydrophilic monomer; maleic anhydride – HEMA adduct*

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Glass ionomer cements and resin-modified glass ionomer cements are known to release substantial amounts of fluoride (1–5). Fluoride release from restorative materials or luting agents is important because of a probable caries inhibitory effect (6–10). The group of materials called compomers has also been found to release fluoride. However, as is the case with fluoride-containing resin composites, the release from compomers is smaller than the release from glass ionomer cements (11–13). The fluoride release from a material is associated with the transport of fluoride ions, which is facilitated by a hydrophilic or ionic environment. But also factors like permeability, surface dissolution, and various intrinsic factors may govern the release of fluoride (14). The polymer matrix of compomers is modified by the presence of carboxylic groups, which render these materials hydrophilic to some degree. In contrast, resin composites have a polymer matrix that is only modestly hydrophilic, which means that the transport of water and ions is restricted. These differences in composition may explain, in part, why compomers release more fluoride than do resin composites (11).

While the caries inhibitory potential of glass ionomer cements is well documented (6–10, 15), only few studies have determined the anticaries effect of fluoride release from compomers and resin composites (16). In order to increase the fluoride release from resin composites, and compomers as well, it would seem to be of interest to

investigate factors which govern this release. A judicious choice of polymer matrix is a conceivable avenue to increase the release in such a way that mechanical properties are not affected (17, 18).

It was the aim of the present work to study the influence of resin matrix formulation on the fluoride release from experimental, fluoride-containing resin composites. We hypothesized that polymer matrices originating from monomer mixtures containing the hydrophilic monomer HEMA (2-hydroxyethyl methacrylate) and a new acidic monomer (HEMAN, to be described below) would give rise to increased fluoride release. A glass ionomer cement and a compomer were included as controls.

Materials and methods

The materials evaluated for fluoride release were a glass ionomer cement (Fuji II, GC, Tokyo, Japan, batch no. (powder) 930901; (liquid) 930701B), a compomer (Dyract, De Trey, Konstanz, Germany, batch no. KL 15.72.2), and a number of experimental resin composites. Two series of resin composites were produced. In the first series, the monomer contained UEDMA (urethane-ethoxy dimethacrylate) and TEGDMA (triethylene glycol dimethacrylate) in the proportion of 75/25 mol/mol. The second series contained UEDMA and HEMA, also in the proportions of 75/25 mol/mol. Since HEMA is miscible with water and

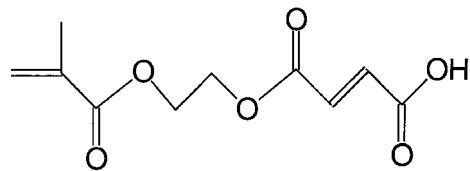


Fig. 1. Structure of the HEMAN monomer used to increase the acidity of the experimental resin composites.

TEGDMA is not, the monomer mixtures (and the resulting polymers) differed with respect to hydrophilicity. To the two series was added a new monomer HEMAN, which is the adduct of maleic anhydride (MAN) and HEMA. To produce HEMAN, equimolar amounts of MAN and HEMA were mixed at room temperature. The reaction between anhydride and the hydroxyl group of the HEMA molecule had come to an end in less than 3 days, as verified by NMR analysis. Fig. 1 shows the structure of the HEMAN molecule. HEMAN was added in amounts of 10, 20, 30, or 40 mol%. The monomer mixtures were then made photosensitive by dissolution of 0.2 w% of camphorquinone and 0.2 w% of cyanoethyl methyl aniline. Two types of filler were then added to the monomer mixture. One type was a silanized glass filler. The other type was fluoride-containing and consisted of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ (97%, Aldrich-Chemie, Steinheim, Germany). The latter type of filler was selected because of the similarity with the aluminum salt of the matrix of glass ionomer cements. The fluoride release from this matrix is known to take place without adverse effects on mechanical properties (17). After mixing, the composite material contained 70 w% of the glass filler and 1 w% or 5 w% of the fluoride-containing filler.

Freshly mixed materials were applied in cylindrical brass molds ($h = 1$ mm, $d = 10$ mm) and covered on both sides with a transparent matrix. The photosensitive materials were irradiated on both sides for 40 s. The matrices were then removed, the specimens freed from the molds and stored at ambient humidity at 37°C for 1 day. Instead, after setting the glass ionomer cement was placed in 100% relative humidity at 37°C for 1 day. Then the matrices were lifted off and the specimens removed from the molds. The disks were polished on both sides on carborundum paper (no. 1000) and each disk then placed at room temperature in a glass vial containing 5.0 ml of distilled water and a magnetic stirrer. The storage medium was agitated continuously throughout the entire experimental period. There were 5 specimens in each series. At predetermined time intervals for up to 3 years, the fluoride concentration in the solution was measured with a fluoride sensitive electrode (Autocal pH METER, fluoride electrode F 1052F; Radiometer, Copenhagen, Denmark) after addition of 10% of TISAB (TISAB III; Merck, Darmstadt, Germany). Calibration curves were produced from solutions containing known amounts of NaF. The cumulative fluoride release was found by addition, and the standard deviations of these values calculated accord-

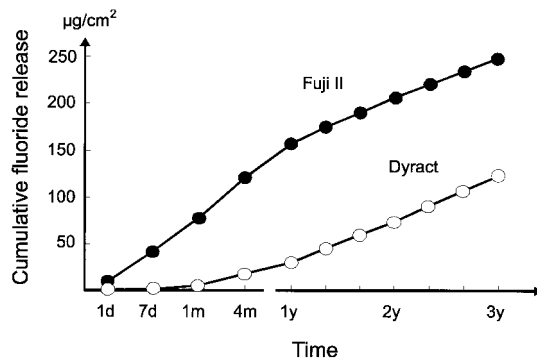


Fig. 2. Cumulative fluoride release ($\mu\text{g}/\text{cm}^2$) from a glass ionomer cement (Fuji II) and a compomer (Dyract) stored in distilled water for 3 years. The standard deviations are about 5% of the mean values, and thus so small that they are contained within each circle.

ing to standard procedures (19). The amount of fluoride released was converted into micrograms per unit surface area of the specimen ($\mu\text{g}/\text{cm}^2$). After each measurement, the specimen was stored in 5 mL of fresh deionized water.

Statistics

When permitted by the homogeneity of variances, the data were treated statistically by analysis of variance, regression analysis, and Newman-Keuls' multiple-range test. In the other case, the Kruskal-Wallis one-way analysis of variance by ranks was used (19–21).

Results

Fig. 2 shows the fluoride release from the glass ionomer cement and the compomer. For the glass ionomer cement, the rate of fluoride release decreased with time during the 1st year and thereafter attained a constant rate. For the compomer, the fluoride release was relatively small initially, but the rate of release increased significantly after a number of months. In the period of time from 12 to 36 months, regression analysis was used to determine the rate of fluoride release, i.e. the slope of the curves depicted in Fig. 2. During this period, the release from the compomer was $0.127 \pm 0.004 \mu\text{g}/\text{cm}^2$ per day and from the glass ionomer cement $0.129 \pm 0.004 \mu\text{g}/\text{cm}^2$ per day. These rates do not differ from each other with statistical significance ($P > 0.05$). Tables 1–3 show the fluoride release from the experimental resin composites. Significant differences at 1 week, and at 12, 24, and 36 months are presented in the Tables. The fluoride release was initially relatively small, but after about a year the rate of release increased appreciably. In the period of time from 12 to 36 months the rate of release from the experimental materials ranged between $0.00140 \pm 0.00007 \mu\text{g}/\text{cm}^2$ per day and $0.050 \pm 0.002 \mu\text{g}/\text{cm}^2$ per day, as determined by regression analysis. The fluoride release increased with the content of HEMAN and with the content of the fluoride-

Table 1. Cumulative fluoride release ($\mu\text{g}/\text{cm}^2$) from experimental resin composites based on UEDMA and HEMA containing 1 w% $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$. (Means \pm SD)

Time	HEMAN (mol%)				
	0	10	20	30	40
1 d	0.6 \pm 0.08	0.6 \pm 0.06	0.6 \pm 0.03	0.5 \pm 0.01	0.6 \pm 0.04
1 wk	^c 0.7 \pm 0.08	^b 0.7 \pm 0.06	^{ab} 0.6 \pm 0.03	^a 0.6 \pm 0.02	^{ab} 0.7 \pm 0.04
1 mo	0.9 \pm 0.08	0.8 \pm 0.06	0.8 \pm 0.03	0.7 \pm 0.02	0.8 \pm 0.04
4 mo	1.0 \pm 0.08	0.9 \pm 0.06	0.9 \pm 0.03	1.1 \pm 0.05	4.2 \pm 0.34
12 mo	^a 1.3 \pm 0.09	^a 1.3 \pm 0.07	^b 1.6 \pm 0.06	^c 2.1 \pm 0.09	^d 6.6 \pm 0.35
16 mo	1.5 \pm 0.09	1.5 \pm 0.08	2.0 \pm 0.14	2.8 \pm 0.13	7.7 \pm 0.39
20 mo	1.6 \pm 0.10	1.6 \pm 0.08	2.3 \pm 0.14	3.3 \pm 0.13	8.7 \pm 0.40
24 mo	^a 1.8 \pm 0.11	^a 1.8 \pm 0.08	^b 2.6 \pm 0.15	^c 3.7 \pm 0.13	^d 9.4 \pm 0.40
28 mo	2.0 \pm 0.11	2.0 \pm 0.09	2.8 \pm 0.16	4.1 \pm 0.14	10.1 \pm 0.41
32 mo	2.3 \pm 0.11	2.3 \pm 0.13	3.2 \pm 0.18	4.8 \pm 0.21	11.0 \pm 0.41
36 mo	^a 2.5 \pm 0.16	^a 2.6 \pm 0.18	^b 3.6 \pm 0.27	^c 5.6 \pm 0.33	^d 12.1 \pm 0.59

For each time, mean values with the same superscript letter do not differ from each other at $P = 0.05$.

containing part of the filler. Although not always with statistical significance, the HEMA-containing resin composites showed a fluoride release that was generally higher than the one from the TEGDMA-containing composites. At 3 years, the cumulative fluoride release was $247 \pm 7 \mu\text{g}/\text{cm}^2$ for the glass ionomer cement, $122 \pm 8 \mu\text{g}/\text{cm}^2$ for the compomer, and ranged from 2.3 ± 0.2 to $79 \pm 6 \mu\text{g}/\text{cm}^2$ for the experimental composites. These values differ from each other with statistical significance ($P < 0.001$).

Discussion

The fluoride release from a glass ionomer cement, a compomer, and a number of experimental resin composites was monitored during the course of 3 years. The pattern of release from the glass ionomer cement, i.e. a significant initial release which diminished with time, has been found in previous studies (2, 5, 11). Likewise, the initial modest release from the compomer has been documented in several earlier studies (11, 22, 23). The long-term data of the present study are in agreement with

a recent study showing that after a certain time in water the rate of fluoride release from compomers approached that of glass ionomer cements (11). The explanation that the fluoride release from compomers increases with time is linked to the diffusion of water into the material. The water is necessary for the formation of hydrogen ions, which by attacking the fluoride-containing glass particles causes a liberation of fluoride. It is not until after a certain period of time that sufficient water has been absorbed into the material to make this reaction take place to an appreciable extent. The amounts of fluoride released by the compomer at 1 d ($0.8 \mu\text{g}/\text{cm}^2$) and at 7 d ($2.7 \mu\text{g}/\text{cm}^2$) are in perfect agreement with the release earlier recorded for the same compomer (24), but at 4 months ($8.6 \mu\text{g}/\text{cm}^2$) are higher than those reported by Karantakis et al. (25). The amounts released by the glass ionomer cement at 1 d ($9.7 \mu\text{g}/\text{cm}^2$) and at 7 d ($41.4 \mu\text{g}/\text{cm}^2$) fall in between earlier determined values (25, 26), and at 4 months ($119 \mu\text{g}/\text{cm}^2$) are higher than that reported by Karantakis et al. (25). The discrepancies may be due to differences between the investigated glass ionomer cements (11) and to differences in experimental conditions. In the present

Table 2. Cumulative fluoride release ($\mu\text{g}/\text{cm}^2$) from experimental resin composites based on UEDMA and TEGDMA containing 1 w% $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$. (Means \pm SD)

Time	HEMAN (mol%)				
	0	10	20	30	40
1 d	0.3 \pm 0.03	0.3 \pm 0.06	0.4 \pm 0.01	0.4 \pm 0.03	0.4 \pm 0.04
1 wk	^{ab} 0.4 \pm 0.03	^a 0.4 \pm 0.06	^c 0.5 \pm 0.02	^c 0.5 \pm 0.03	^{bc} 0.5 \pm 0.04
1 mo	0.6 \pm 0.04	0.8 \pm 0.09	0.8 \pm 0.02	0.7 \pm 0.04	0.6 \pm 0.04
4 mo	0.8 \pm 0.04	0.9 \pm 0.09	1.0 \pm 0.03	1.0 \pm 0.04	2.1 \pm 0.18
12 mo	^a 1.2 \pm 0.07	^a 1.3 \pm 0.10	^b 1.6 \pm 0.05	^c 2.0 \pm 0.05	^d 3.3 \pm 0.19
16 mo	1.5 \pm 0.08	1.4 \pm 0.10	2.1 \pm 0.08	2.8 \pm 0.06	4.1 \pm 0.25
20 mo	1.7 \pm 0.08	1.5 \pm 0.10	2.4 \pm 0.08	3.3 \pm 0.07	4.7 \pm 0.25
24 mo	^a 1.9 \pm 0.09	^a 1.7 \pm 0.10	^b 2.7 \pm 0.09	^c 3.7 \pm 0.08	^d 5.2 \pm 0.25
28 mo	2.1 \pm 0.09	1.9 \pm 0.10	2.9 \pm 0.09	4.0 \pm 0.08	5.7 \pm 0.25
32 mo	2.5 \pm 0.15	2.1 \pm 0.11	3.3 \pm 0.10	4.5 \pm 0.09	6.4 \pm 0.26
36 mo	^b 2.8 \pm 0.23	^a 2.3 \pm 0.16	^c 3.6 \pm 0.15	^d 4.9 \pm 0.14	^e 7.1 \pm 0.38

For each time, mean values with the same superscript letter do not differ from each other at $P = 0.05$.

Table 3. Cumulative fluoride release ($\mu\text{g}/\text{cm}^2$) from experimental resin composites based on UEDMA and TEGDMA containing 5 w% $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$. (Means \pm SD)

Time	HEMAN (mol%)				
	0	10	20	30	40
1 d	5.7 \pm 0.7	7.0 \pm 0.7	7.5 \pm 0.5	8.5 \pm 0.7	8.2 \pm 1.3
1 wk	^a 6.2 \pm 0.7	^{ab} 7.4 \pm 0.7	^{bc} 7.9 \pm 0.5	^c 8.9 \pm 0.7	^{bc} 8.6 \pm 1.3
1 mo	6.6 \pm 0.7	7.7 \pm 0.7	8.1 \pm 0.5	9.3 \pm 0.7	9.4 \pm 1.4
4 mo	7.2 \pm 0.7	8.3 \pm 0.7	9.1 \pm 0.6	11.6 \pm 0.8	29.0 \pm 3.7
12 mo	^a 8.2 \pm 0.8	^b 9.0 \pm 0.7	^c 10.6 \pm 0.6	^d 16.6 \pm 0.9	^c 41.7 \pm 3.9
16 mo	8.9 \pm 0.8	9.9 \pm 0.8	12.6 \pm 0.8	20.7 \pm 0.9	49.2 \pm 3.9
20 mo	9.6 \pm 0.8	10.6 \pm 0.8	14.5 \pm 1.2	23.7 \pm 1.0	55.7 \pm 4.0
24 mo	^a 10.3 \pm 0.8	^a 11.2 \pm 0.8	^b 15.9 \pm 1.3	^c 26.6 \pm 1.0	^d 60.5 \pm 4.0
28 mo	10.9 \pm 0.9	11.9 \pm 0.9	17.1 \pm 1.3	29.2 \pm 1.1	65.3 \pm 4.0
32 mo	11.6 \pm 0.9	13.4 \pm 1.0	19.1 \pm 1.5	33.6 \pm 1.3	73.2 \pm 4.2
36 mo	^a 12.5 \pm 1.4	^a 14.2 \pm 1.5	^b 20.5 \pm 2.1	^c 36.9 \pm 1.8	^d 78.9 \pm 6.0

For each time, mean values with the same superscript letter do not differ from each other at $P = 0.05$

study, for example, a magnetic stirrer was used, while in the studies just cited the specimens were kept in a non-agitated storage media.

The experimental resin composites showed a release pattern similar to that of the compomer. As was the case with the compomer, absorption of water into the material is necessary to set free the hydrogen ions capable of attacking the fluoride-containing filler particles. It is in agreement with several earlier studies (e.g. 11, 25) that the amount of fluoride released from resin composites was smaller than that released from glass ionomer cements and compomers. However, Temin and Csuros found that a specially designed resin composite was able to release considerable amounts of fluoride (26). With this commercial, fluoride-containing resin composite, a relatively constant release rate of about $0.20 \mu\text{g}/\text{cm}^2$ per day was reached after about a year. This is higher than the rates for glass ionomer cement ($0.129 \mu\text{g}/\text{cm}^2$ per day) and the compomer ($0.127 \mu\text{g}/\text{cm}^2$ per day) of the present study, and also higher than that found for the experimental resin composites (0.001 to $0.050 \mu\text{g}/\text{cm}^2$ per day). Obviously, the fluoride contained in the resin composite studied by Temin and Csuros (26) was present in a particularly available form.

The positive influence of HEMA on the fluoride release may be explained by the increase in hydrophilicity of the polymer matrix. Increasing hydrophilicity facilitates the transport of water and ions, in this case both the hydrogen and the fluoride ion. The finding (Table 1 versus Table 2) that there were only small differences between the HEMA- and the TEGDMA-containing resins at low contents of HEMAN may be explained by a high degree of polymerization of resins containing the monomethacrylate HEMA (27, 28). A high degree of polymerization will impede the transportation of ions in the resin matrix.

HEMAN, like HEMA, had a positive effect on the fluoride release. For example, at 36 months the materials based on resins containing 20, 30, or 40 mol% HEMAN had released significantly more fluoride than materials without HEMAN or with 10 mol% HEMAN. Part of the

explanation may be found in the fact that also HEMAN is a hydrophilic molecule which will allow for the transportation of water and ions in the resin matrix. Materials based on resins containing only 10 mol% of HEMAN showed a fluoride release that was close and in many cases not statistically different from that of materials without HEMAN (Tables 1–3). As was the case with HEMA, this may be due to the fact that also HEMAN is a monomethacrylate and will cause a high degree of conversion of the double bonds. As a consequence, the polymer structure will be more compact, and thus reduce the transportation of water and ions. Another reason for the increase in fluoride release with increasing content of HEMAN may be found in the acidity of the HEMAN molecule. The higher the acidity of the resin matrix, the stronger the attack on the fluoride-containing filler particles, and the higher the fluoride release will be. The resin composites containing 5 w% $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ released more fluoride than the corresponding resins containing only 1 w% $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$. The finding that the increase in fluoride release was not just 5-fold in all series is difficult to explain, but may reflect the complicated nature of absorption and diffusion processes.

All of the experimental resin composites released substantially less fluoride than not only the glass ionomer cement, but also the compomer. Presumably, $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ is not as soluble in the acidic matrix as are the glass particles of the compomer. Another choice of fluoride source than $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ might have increased the fluoride release. However, it is not well established what level of fluoride from a restorative material will cause a significant reduction in caries incidence. The values after 1 month presented in Fig. 2 and in Tables 1–3 are significantly smaller than the value of about $200 \mu\text{g}/\text{cm}^2$ earlier established as necessary completely to inhibit enamel demineralization (29). It cannot be ruled out, however, that a release smaller than that of compomers may be sufficient, perhaps not to inhibit but to give rise to a reduction in caries frequency.

Returning to the hypothesis expressed in the introduc-

tion, it was found that the fluoride release of the experimental resin composites increased with the hydrophilicity and the acidity of the polymer matrix. An increase in the hydrophilic and the acidic character of the matrix will to a higher degree allow for the passage of water and fluoride ions liberated by fluoride-containing components incorporated in the matrix. While glass ionomer cements increase in strength with time in water (17), mechanical properties of compomers may deteriorate significantly (18, 30). It remains to be seen what the effect of prolonged contact with water is on mechanical properties of the HEMAN-containing resin composites. Increased hygroscopic expansion due to the increased hydrophilicity of the material may also be a matter of concern.

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