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Fluoride Release From a New Glass-ionomer Cement

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Clinical Relevance

The antibacterial and cariostatic properties of glass-ionomer cements are associated with the amount of fluoride released. Therefore, fluoride release from a restorative material for extended periods of time is considered favorable.

ABSTRACT

This study compared the amount and pattern of fluoride release from a new glass-ionomer-based material (nano-ionomer) with other restorative materials and correlated the surface area to volume of nano-sized filler with its capacity to release fluoride in the powder, more quickly increasing the fluoride. The materials evaluated were a nano-ionomer (Ketac N 100), a conventional glass-ionomer cement (GC Fuji II), a resin-modified glass ionomer cement (GC Fuji II LC), a compomer (Dyract F) and a fluoride-releasing resin composite (Tetric N Flow). A resin composite (Synergy Flow) served as the control. Ten specimens were fabricated from each of these materials using a customized metal mold. The fluoride release was measured every 24 hours for the first seven days, and on days 14, 21 and 28, a combination fluoride ion—selective electrode connected to an ion analyzer. The data was analyzed by one-way ANOVA and Tukey HSD test (*p*=0.05). An initial fluoride "burst effect" was seen with all of the materials, except for the control and compomer. The conventional glass-ionomer cement showed the highest fluoride release on the first three days. The nano-ionomer showed the maximum release of fluoride for the remaining days. A low constant level of fluoride release was seen from the compomer and fluoride-releasing resin composite throughout the study period.

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INTRODUCTION

The quest to develop an ideal restorative material has led to the development of newer materials and the modification of existing ones. One such material is glass-ionomer cement (GIC), developed by Wilson and Kent in 1972.[1] This material has undergone continuous improvement in its properties and has become popular as a restorative material due to its adhesion and ability to release fluoride.

One of the common causes for the post-operative failure of restorations is secondary or recurrent caries.[2] Delbem and others reported that the initiation and propagation of secondary caries is significantly reduced when glass-ionomer cements are used, due to the release of fluoride.[3] Furthermore, the extent of antibacterial and cariostatic properties of glass ionomer restorative materials is associated with the amount of fluoride released.[4]

The anticariogenic effects of fluoride may be due to several mechanisms. Fluoride taken up by the tooth reduces demineralization and enhances remineralization. Fluoride ions also play a role in the interference of pellicle and plaque formation and the inhibition of microbial growth.[5] Fluoride ions are released during the acid-base reaction of the cement and they are not an essential part of the matrix formation. Hence, they are free to move in and out of the cement.[6] Thus, GIC is considered to be a fluoride reservoir, maintaining a steady flow of fluoride ions into the surrounding tooth structure and enhancing resistance to caries attack throughout the life of the restoration.[7] *In-vitro* studies have shown that glass-ionomer cements can serve as rechargeable reservoirs, delivering a constant low level of fluoride due to uptake from fluoridated solutions, dentifrices and mouthwashes.[7-9]

The setting chemistry of glass-ionomer cement is an acid-base reaction between the polyalkenoic acid and fluoride containing aluminosilicate glass.[1] The fluoride ions are released during the acid base reaction. The amount of fluoride release has been found to vary with the different types of restorative materials, based on their composition, the nature of fluoride incorporated, setting reaction and structure of the set cement. Various media (deionized water, artificial saliva and lactic acid) have been used for measuring the amount of fluoride released.[10-11] Despite the desirable property of fluoride-release, conventional glass ionomers have several disadvantages, such as water sensitivity, poor strength and low occlusal wear resistance. The high sensitivity of these cements to water causes erosion of the glass ionomers during the early setting period, and this further increases the elution of fluoride. The quantitative leaching of fluoride is increased by the presence of cracks and pores on the surface of the material, leaving behind a low amount of residual fluoride.[12-13]

These poor qualities of conventional GIC have led to the development of newer fluoride-releasing materials, including resin-modified glass-ionomer cement, polyacid-modified composites (compomers), giomers and resin composites.[14] Recently, a new material, a nano-ionomer, was introduced. Its manufacturer has indicated that the nano-ionomer has a higher fluoride release. The nano-ionomer is based on acrylic and itaconic acid copolymers necessary for the glass-ionomer reaction with fluoroaluminosilicate (FAS) glass and water. The nano-ionomer also contains a blend of resin monomers, bisphenol A glycidyl metharylate (Bis GMA), triethylene glycol dimethacrylate (TEGDMA), poly ethylene glycol dimethacrylate (PEGDMA), and hydroxyethyl methacrylate (HEMA) which polymerize via a free radical addition polymerization. The origin of this glass-ionomer cement is the inclusion of nano-fillers, which constitute up to two-thirds of the filler content. The presence of nano-sized glass particles and clusters of nanosilica particles in this material has been claimed to improve its physical properties. Nano-ionomer has a structural morphology that is a hybrid of resin-modified glass ionomer and nano-filled resin composite. The manufacturer claims that the acid reactive glass fillers and methacrylate functional nanofillers of the nano-ionomer are smaller than those of conventional resin-modified glass-ionomer cement. It is possible that the nano-sized filler is unique in that, with its increased surface area to volume, it has the capacity to provide a more quicker release of fluoride.

An extensive review of the literature yielded no documentation on the amount and pattern of fluoride release of this material. It is possible that the increased surface area to volume of the nano-sized filler has the capacity to release fluoride in the powder more quickly, increasing the fluoride release of the material. The current study compared the amount and pattern of fluoride release of a nano-ionomer, a conventional glass-ionomer cement, a resin-modified glass-ionomer cement, a compomer and a resin composite using a fluoride ion-selective electrode with ion analyzer. The null hypothesis was that the weekly and cumulative fluoride release of the nano-ionomer was not significantly different from the other materials tested.

METHODS AND MATERIALS

Sixty specimens measuring 5 mm in diameter and 2 mm thick were prepared from six different materials (n=10) by packing the material into a custom metal mold. The materials are listed below and the composition of the materials is summarized (Table 1).

Group I (GIC)–Conventional glass ionomer

Group II (RMGIC)–Resin-modified glass ionomer

Group III (Nano)–Nano-ionomer

Group IV (CP)–Compomer

Table 1: *Materials Used in This Study*

Material	**Composition**	**Manufacturer, Lot Number and Shade**
Group I–Glass ionomer cement	Powder: Calcium fluoroaluminosilicate glass, polyacrylic acid powder, iron oxide Liquid: Polyacrylic acid (aqueous solution), tartaric acid, water	Fuji II, GC America, Alsip, IL, USA; Lot #0707191/22; Shade: Yellow brown
Group II–Resin-modified glass ionomer cement	Powder: Fluoroaluminosilicate glass, shade pigments Liquid: Polyacrylic acid, 2-Hydroxyethyl methacrylate, 2,2,4 Trimethyl hexamethylene dicarbonate, Triethylene glycol dimethacrylate, proprietary ingredient	Fuji II LC, GC America, Alsip, IL, USA; Lot #0612121; Shade: A2
Group III–Nano-ionomer	Paste A: Fluoroaluminosilicate glass, silane-treated silica and zirconia silica nanofillers, methacrylate and dimethacrylate resins, and photoinitiators Paste B : Polyalkenoic acid copolymer, silane-treated zirconia silica nanoclusters, silane-treated silica nanofiller, and hydroxy-ethyl methacrylate	Ketac N 100; 3M ESPE, St Paul, MN, USA; Lot #20070912; Shade: A2
Group IV–Compomer	Urethane dimethacrylate, diester resin of hydroxyethyl methacrylate and butane tetracarboxylic acid, alkanoyl poly-methacrylate, strontium fluoroalumino silicate glass, photoinitiators, iron oxide pigments, strontium fluoride	Dyract F, Dentsply DeTrey, Konstanz, Germany, GmBH; Lot #0708000233 ; Shade: A2
Group V–Fluoride releasing resin composite	Bisphenol A glycidyl methacrylate, urethane dimethacrylate, triethylene glycol dimethacrylate, barium glass, ytterbium trifluoride, highly dispersed silica, mixed oxides, catalysts, stabilizers, pigments	Tetric N flow, Ivoclar Vivadent, Schaan, Liechtenstein; Lot #606957; Shade: A2
Group VI–Control (Resin composite)	Methacrylates, silanized barium glass, hydrophobic amorphous silica	Synergy Flow, Coltène Whaledent, Altstatten, Switzerland; Lot #0140535; Shade: A2/B2

Group V (RC)–Fluoride-releasing resin composite

Group VI (Control)–Resin composite

A matrix Mylar strip (0.08 mm, Mylar Type D, DuPont, Wilmington, DE, USA) was first secured on a glass slide to form the base of the mold. The restorative material was then mixed according to the manufacturer's instructions and placed in the mold. The mold was then covered with a second Mylar strip. A glass slide was placed over this mold and pressure was applied to extrude the excess material. The conventional glass ionomer was allowed to set at room temperature for 15 minutes. The resin-modified glass-ionomer, nano-ionomer, compomer and resin composite specimens were cured through the glass slide with an Elipar 2500 (3M ESPE, St Paul, MN, USA) halogen curing unit. The intensity of the light source was checked with a radiometer prior to the study and before each specimen was cured. An output of 540mW/cm^2 was confirmed. The output, which was checked after illumination through the glass slide and Mylar strip, remained unaltered. The specimens were cured according to the manufacturers' instructions. The resin-modified glass-ionomer, nano-ionomer and resin composite specimens were light cured for 20 seconds. The compomer was cured for 40 seconds. The light-cured specimens were cured from both sides of the mold. All of the materials were stored at 95% relative humidity and 37°C for 24 hours to allow them to set completely.

All of the specimens were then polished (Sof-Lex, 3M ESPE) to remove the resin rich surface layer (which may increase the fluoride release rate), and each specimen was immersed in 5 mL buffered deionized water (pH=7) in a small air tight polyethylene vial at 37°C. After 24 hours, the vials were thoroughly shaken and the water removed and analyzed. The specimens were then re-immersed in 5 mL of fresh deionized water. The amount of fluoride released was studied every 24 hours for the first week, then subsequently at 14, 21 and 28 days. Each water sample was buffered with total ionic strength adjustment buffer (TISAB III), and the fluoride analysis was carried out using a combination fluoride ion-selective electrode (Model 96-09-BN, Orion Research Inc, Boston, MA, USA) connected to an Orion ion analyzer (Model EA 940, Orion Research Inc). The results were tabulated and the mean and standard deviation values were estimated for each study group. The mean values among the different study groups were compared using one-way ANOVA to determine the level of significance. In the current study, $p<0.05$ was considered to be the level of significance. The Multiple-range Tukey's HSD test was used to identify the significant groups ($p=0.05$).

RESULTS

The values of fluoride release were tabulated as Mean ± Standard deviations. The results of the current study showed that, on days 1, 2 and 3, the mean value of fluoride release of GIC was the highest, followed by Nano, RMGIC and CP; the lowest mean value was seen in RC (Table 2). All of the materials showed the highest

Table 2: *Mean Fluoride Release (µg/dl/mm^2) During the First Week*

Group	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
GIC	11.5 ± 1.70^{a}	7.7 ± 0.07^{a}	6.6 ± 0.21^{a}	6.3 ± 0.05^{a}	4.5 ± 0.09^{a}	3.1 ± 0.06^{a}	1.5 ± 0.21^{a}
RMGIC	7.2 ± 0.62^{b}	5.8 ± 0.06^{b}	6.1 ± 0.06^{b}	7.1 ± 0.12^{b}	7.1 ± 0.09^{b}	5.1 ± 0.24^{b}	2.1 ± 0.12^{b}
Nano-ionomer	7.9 ± 0.11^{b}	6.7 ± 0.23^{b}	6.6 ± 0.08^{a}	7.3 ± 0.19^{c}	7.6 ± 0.07^{c}	5.4 ± 0.18^{c}	2.9 ± 0.15^{c}
Compomer	4.2 ± 0.21^{d}	2.1 ± 0.04^{d}	2.5 ± 0.10^{d}	2.4 ± 0.19^{d}	1.8 ± 0.08^{d}	1.5 ± 0.09^{d}	1.5 ± 0.08^{d}
Resin Composite	1.5 ± 0.08^{e}	1.1 ± 0.06^{e}	0.9 ± 0.06^{e}	0.9 ± 0.12^{e}	1.0 ± 0.11^{e}	0.9 ± 0.10^{e}	0.7 ± 0.11^{e}

**Different letters (for each day) imply significantly different groups (p<0.05).*

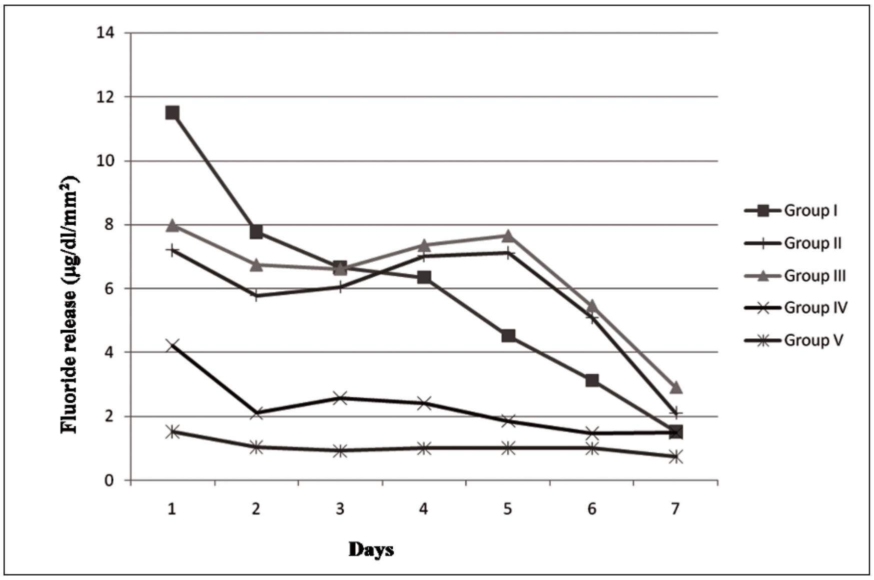

Figure 1. *Pattern of fluoride release during the first week (x-axis: Days; y-axis: Fluoride release in µg/dl/mm^2).*

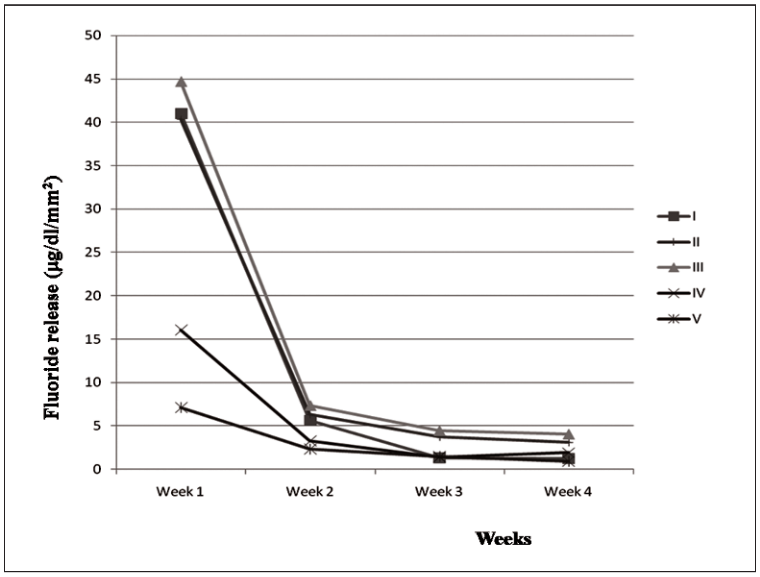

Figure 2. *Pattern of fluoride release for 28 days (x-axis: Weeks; y-axis: Fluoride release in µg/dl/mm^2).*

amounts of fluoride release on days 1 and 2 (Figure 1). There was a significant difference among the different groups in the mean values of fluoride release on days one and two (one-way ANOVA; $p<0.05$). In the same time period, it was found that the mean value of fluoride release from GIC was significantly higher than the values of Nano, RMGIC, CP and RC (Tukey HSD; $p<0.05$). However, there was no significant difference in mean values between RMGIC and Nano ($p>0.05$). The control group (resin composite) showed no detectable amounts of fluoride release and is not included in the table or graphs.

The weekly fluoride release of GIC, RMGIC and Nano exhibited a sharp drop from the first week, to a constant low level in weeks three and four. The curves depicting the pattern of fluoride release of GIC, RMGIC and Nano were parallel to each other, with Nano showing the highest release. CP and RC showed a low but constant level of fluoride release throughout the study period (Figure 2). The cumulative fluoride release at the end of the study period in GIC, RMGIC and Nano, was significantly higher than CP and RC ($p<0.05$; Table 2 and Figure 3). At weeks one and two, no statistically significant difference was seen between GIC and RMGIC. A statistically significant difference was observed among all the groups in the third and fourth weeks ($p<0.05$).

DISCUSSION

The initial fluoride release from glass ionomer is due to an acid-base reaction, with the amount of fluoride released proportional to the concentration of fluoride in the material.[5] This is responsible for the phenomenon of "burst effect," wherein high amounts of fluoride are released during the first two days.[3,5,10-12] Fluoride release declines rapidly during the first week and stabilizes after three to four weeks.[12-15] Caries lesions adjacent to the restoration are likely to take from several months to several years to develop. To prevent these lesions from developing, the fluoride must be released for long periods of time.

The use of deionized water to determine fluoride release has been suggested by several investigators.

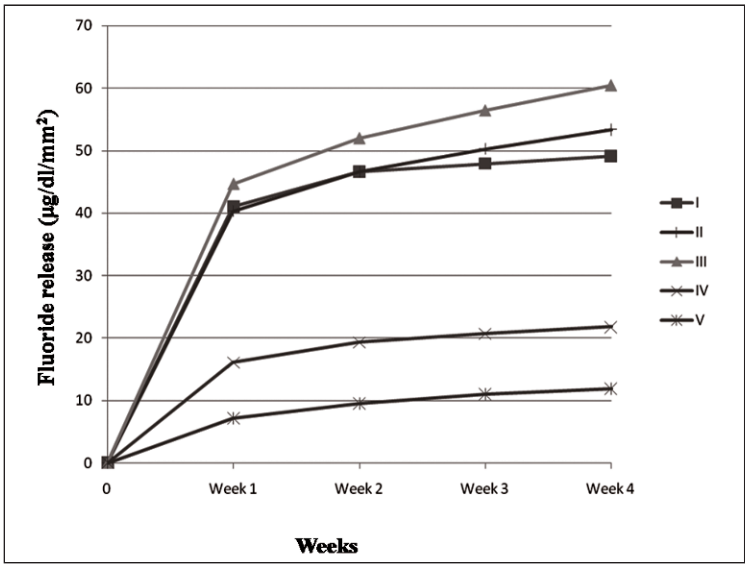

Figure 3. *Pattern of cumulative fluoride release (x-axis: Weeks; y-axis: Fluoride Release in µg/dl/mm^2).*

Since there are no existing ions in this medium, the use of deionized water is considered as giving an accurate estimate of the fluoride ions released. This view is endorsed by other authors.[16-17] Both a reduced and a higher release of fluoride have been identified when artificial saliva[16] and acidic media[11] have been used, respectively. It is possible that removing and refreshing the medium every time may temporarily change the diffusion gradient and accelerate the fluoride release. The determination of fluoride release is based on a concentration gradient mechanism and the release is stopped when equilibrium is attained.[17] The protocol followed in the current study was to change the water at a minimum interval of 24 hours, as recommended by other authors.[9,15]

The methods that have been employed to estimate the amount of fluoride release include spectrophotometry, ion chromatography, capillary electrophoresis and fluoride ion-selective electrodes with an ion analyzer.[12] An ion specific electrode connected to an ion analyzer is an accurate and established method of determining fluoride release. This method gives a direct estimate of the free fluoride present.[12-13,16] However, fluoride compounds cannot be estimated by this method.[12]

The results of the current study showed parallel fluoride release curves for conventional and resin-modified glass ionomers. During the first two days, resin-modified glass ionomer released less fluoride than the conventional glass ionomer. This finding of the current study is in agreement with the findings of Vermeersch and others.[13] However, resin-modified glass ionomers showed significantly greater cumulative and long-term fluoride release. The HEMA present in resin modified glass ionomers slowly absorbs water to allow for the diffusion of fluoride ions.[3] This fluoride is released gradually, thereby explaining the higher long-term release over a one month period when compared to the conventional glass-ionomer cement.

The null hypothesis, that there was no significant difference between the weekly and cumulative fluoride release of nano-ionomer and the other materials tested in the current study, was rejected. In the current study, the fluoride release from the nano ionomer at the end of the first week (44.69 µg) and its cumulative fluoride release (60.48 µg) was the highest among all the groups studied. GIC, RMGIC and Nano showed a high amount of fluoride release during the first three days. This pattern may be explained by the rapid elution of fluoride liberated as a result of the acid base reaction, which takes place on the surface of the glass particles.[5,11]

At week four, Nano and RMGIC released approximately 4 µg and 3 µg of fluoride, while conventional glass ionomer and compomer released 1 µg and resin composite released no fluoride. The authors of the current study speculate that the smaller sized glass particles, called "nanomers," may play a significant role in this regard. It has been reported that the smaller glass particles provide a larger surface area, which increases the acid-base reactivity, and hence, has the capacity to release fluoride from the powder more quickly, increasing the fluoride release of the material.[5,13]

The amount of fluoride released from the compomer was lower than with the conventional GIC, resin-modified GIC and nano-ionomer. This is in accordance with other reports.[13,16,19] No burst effect of fluoride release was identified with compomers, and the amount of release remained marginally higher than resin composite. These materials have no auto-setting acid-base reaction typical of conventional glass ionomers. Only light-cured polymerization occurs to form the polymer resin matrix in which unreacted glass particles are present that contain a low amount of fluoride. The fluoride release is caused by the absorption of water after the initial photo-activated radical polymerization. The penetration of water plays a crucial role in fluoride release. However, water sorption caused degradation of the filler particles, resulting in loss of strength and erosion of the material.[13,21]

Fluoride-releasing composites contain ytterbium trifluoride fillers. The fluoride release from these materials was found to be the least during the first week (1.51 µg on the first day and 0.73 µg on the seventh day). The cumulative fluoride release of 11.88 µg at the end of 28 days was also the lowest among the groups studied. The constant low level of fluoride release observed from RC (group V) confirms the results obtained in several studies.[4,9,11,13] The fluoride release from these materials is not a function of the setting reaction but due to the passive leaching that may occur from the fluoride-containing filler particles.[4,22] The low release may be due to the low amount of fluoride incorporated in these materials as fillers, the low solubility of ytterbium trifluoride in water,[11] the low water content of the material and the permeability of the resin composite.[16,22]

CONCLUSIONS

Within the limitations of this *in vitro* study, it may be concluded that cumulative fluoride release at the end of the study period in nano-ionomer, glass ionomer cement and resin-modified GIC was significantly higher than compomer and resin composite ($p<0.05$). This is possibly due to the different nature of the filler in nano-ionomer. Further research is needed regarding this. In the oral cavity, fluoride is not completely washed away, and a subsequent uptake of fluoride is possible. Therefore, it may not be possible to directly extrapolate these results to the clinical scenario. Further long-term studies and clinical trials are required to substantiate the results and evaluate its fluoride recharging characteristics.

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