

FLUORIDE RELEASE AND UPTAKE BY GLASS IONOMER CEMENTS, POLYACID MODIFIED COMPOSITE RESIN AND GIOMER- AN IN VITRO ASSESSMENT

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ABSTRACT

Aim: The purpose of this study was to evaluate the release of fluoride ions from Glass ionomer cements, Giomer and Polyacid-modified composite resin (Compomer) and to compare their fluoride uptake after application of topical fluoride agents: APF gel and NaF gel.

Material & Methods: A total number of 40 specimens of four fluoride releasing dental restorative materials were fabricated of size 5 mm in diameter x 2 mm in height, using a teflon mould and were randomly divided into four groups. These specimens were immersed in 10 ml of artificial saliva and the amount of fluoride released was measured on 1st (24 hrs), 3rd, 7th & 14th day. On 14th day all the specimens of each group were divided into two sub- groups of 5 specimens each and placed in 2ml of APF gel & 2ml of NaF gel for 4 minutes for recharge of these materials and again the release of fluoride from recharged specimens was estimated. **Result:** The amount of fluoride released from the various materials was significantly different. The highest release was shown by the Fuji IX followed by Ketac molar, polyacid-modified composite resin (Compomer) and Giomer.

KEYWORDS: Fluoride; glass ionomer cements; composite resin; giomer

INTRODUCTION

Dental caries is a disease in response to complex interaction between biofilm and its environment, in which demineralization of tooth surfaces may

ultimately result in cavity formation. This process is affected by various modifying factors ie the quality and quantity of saliva, fluoride and other remineralising agents.^[1-11] Fluoride has been found to be effective in inhibiting the demineralization process while favouring the remineralization process by increasing enamel resistance to dissolution by acid produced by bacterial.^[12] Delivery of fluoride is accomplished by several means, most commonly by fluoridation of public water supplies, fluoridated dentifrices, mouth rinses and consequently, development of restorative materials that facilitate constant delivery of fluoride directly to the susceptible tooth surfaces. It is reported by Kidd (1992)^[14] and Arends (1995)^[11] that approximately half of all restorative dentistry work is in the form of replacement of restorations, and about 60% of replacements are attributed to secondary caries. This lead to introduction of new restorative materials in the last decades with fluoride releasing property aimed at inhibiting recurrent decay. Henceforth extensive amount of work has been performed to evaluate fluoride release from restorative materials and recharge ability of these materials.^[15-25] One such group of material is the "Glass Ionomer" introduced by Wilson and Kent (1972)^[26] which has important properties, such as chemical bonding to tooth structure and biocompatibility, well balanced physical properties, and antimicrobial activity with shortcomings, like, sensitive to moisture contamination and esthetics, which make them second choice to resin composites. In the 1990s resin-modified glass ionomers was developed by Mathis and

Table 1

Product	Manufacturer	Group No
Fuji IX - GC gold label Posterior Restorative	GC Corporation Japan	I
Ketac Molar Easymix	3M ESPE, Germany	II
Giomer -Beautifil II	SHOFU INC. Kyoto, Japan	III
Compomer-Dyract Extra	DENTSPLY, Germany	IV
APF gel 1.23%	Pascal Company, WA, USA	
NaF gel 2.71%	Septodent Company ,France	

Ferracane (1989).^[15] They retain many of the glass ionomer's beneficial properties, such as long-term fluoride release and the ability to be recharged with topically applied fluoride with better esthetic and handling characteristics. But resin-modified glass ionomers later found to get discoloured over the time as compared to composites as observed by McCabe (1998).^[16] In early 1990's polyacid modified resin composite "Compomers" were developed which combine the best properties of glass ionomers and composite resins. They have better esthetics, easier to place and polish, are radiopaque and show higher bond strength than resin modified glass ionomer cements. Although they being better than GICs, they release less fluoride and could not be recharged. In the continuing quest for improved glass ionomer-like restoratives, manufacturers have developed and introduced a new class of materials called "Giomers." They are a hybrid of "glass ionomer" and "composite". They have properties of both glass ionomers (fluoride release, fluoride recharge) and resin composites (excellent esthetics, easy polishability, biocompatibility). Giomers are distinguished by the fact that, while they are resin-based, they contain pre-reacted glass-ionomer (PRG) particles. The particles are made of fluorosilicate glass that has been reacted with polyacrylic acid prior to being incorporated into the resin. Giomers have inherent property of fluoride release over a period of time with recharging property as noticed by Itotaa(2004),^[13] Dhull(2009)^[6] which is the most important property in terms of caries prevention. The aim of this study was therefore, to examine the fluoride releasing and recharging ability of glass ionomer and resin based materials containing fluoridated glass filler and comparing the recharging ability of these materials after exposure to topical fluoride, as above mentioned materials have very less supportive scientific research.

MATERIALS & METHODS

The materials used for this study were two conventional glass ionomer cement, one polyacid-modified composite resin (Compomer) and one Giomer (Table 1). Total number of 40 specimens were made and randomly divided into four group consisting of 10 specimen each using teflon mould of size 5 mm in diameter x 2 mm in height. The materials were placed into the mould covered on each side with a polyester strip and a glass slide. Glass ionomer cements (Fuji IX, Ketac Molar), were mixed according to the manufacturer's instructions and allowed to set for 10 min in the mould, while Giomer (Beautifil II), Compomer (Dyract Extra) were light cured using Dentsply light curing unit. The prepared discs were subjected to thermal cycling (500 cycles) at 5⁰C- 37⁰C - 55⁰C with dwell time of 15 seconds in controlled water bath. The artificial saliva was prepared according to Macknight Hane and Whitford (1992) ^[17] formula and the specimens were immersed in artificial saliva. The artificial saliva was changed on daily basis to avoid fluoride saturation of the solution. The release of fluoride in artificial saliva was estimated before application of topical fluoride on 1st, 3rd, 7th and 14 day. On 14th day each group was further divided into two subgroups of 5 specimens each and two topical fluoride ie APF gel and NaF gel were applied for 4 min and washed with distilled water to remove the residual material. Again estimation of fluoride was done for next 14 days at predetermined days. To determine the amount of fluoride release, 1 ml of TISAB III was mixed in 10 ml of sample solution. Fluoride ion analysis was performed by ion selective electrode method using expandable ion analyzer (Thermo Orion model 96-09) and combination fluoride electrode. In each session, the electrode was calibrated with serially standard fluoride solutions containing 0.1, 1, 10, 100 ppm fluoride, diluted with 10% v/v TISAB III. The fluoride concentration of the

solutions were separately measured for each sample on day 1,3,7 and 14th day.

RESULTS

Mean Fluoride Release before recharge at day1st, 3rd, 7th and 14th for all four groups, indicated that at all the time intervals group I showed maximum fluoride release with mean value 0.333 ± 0.037 ppm on day 1 whereas group III showed minimum fluoride release with mean value 0.172 ± 0.010 ppm. It was observed that with passage of time there was decrease in amount of fluoride release in all the four groups. Maximum fluoride release on day 14 was observed to be 0.075 ± 0.013 ppm for group I whereas minimum fluoride release was observed to be 0.035 ± 0.006 ppm for group III. A statistically significant difference among the groups for fluoride release was seen at all time intervals ($p < 0.001$). Group I > Group II > Group IV > Group III. On recharge with APF show, group I had the maximum mean fluoride (1.096 ± 0.126 ppm) release while group III had the minimum fluoride (0.137 ± 0.016 ppm) release 24 hours after recharging. With passage of time, a continuous decrease in fluoride release was observed in all groups. While on recharge with NaF mean fluoride release in different groups at all the time intervals, group I had the maximum value (0.529 ± 0.149 ppm, 0.351 ± 0.103 ppm, 0.192 ± 0.018 ppm, 0.029 ± 0.009 ppm respectively) whereas group III had minimum value (0.134 ± 0.028 ppm, 0.118 ± 0.019 ppm, 0.070 ± 0.022 ppm, 0.021 ± 0.004 ppm respectively) on all days compared to other groups. With passage of time, a decrease in mean fluoride levels was observed in all the four groups. The intra group comparisons of fluoride release before and after recharge with topical fluoride APF/NaF with respect to time, in group I & II mean fluoride release on day 1 before recharging in 10 samples was of lower order as compared to after recharging with APF and NaF. Maximum fluoride release was found when samples were recharged with APF than with NaF. The intra group comparisons of fluoride release in group III, mean fluoride release on day 1,3,14 was higher in before recharge samples than samples recharged with NaF and APF. While on day 7 recharged samples with APF and NaF both was higher release of fluoride than before recharged samples but this difference was found to be

statistically significant only for APF samples. In case of group IV on day 1 the samples recharged with APF & NaF showed significantly higher fluoride release than that of before recharge samples. While on day 3 the samples recharged with APF showed a higher fluoride release than samples recharged with NaF and the before recharge samples. On day 7 the mean fluoride release was found to be significantly higher for recharged samples APF and NaF both as compared to before recharge. While on day 14, both the recharged samples with APF and NaF showed lesser fluoride release (mean 0.021 ± 0.003 ppm & 0.029 ± 0.014 ppm respectively) than before recharge samples (baseline) value (0.050 ± 0.003 ppm), but the results were not found to be significant statistically.

DISCUSSION

The aim of this study was therefore, to examine the fluoride releasing ability of glass ionomer and resin based materials containing fluoridated glass filler and comparing the recharging ability of these materials after exposure to topical fluoride. In the present study artificial saliva was used as a specimen storage solution so as to simulate an environment similar to oral cavity for fluoride release. The artificial saliva was changed every day in the present study to prevent saturation of the solution as reported by Yap *et al.*,^[28] who noticed that frequency of change of the storage media is a critical factor and storage for more than 24 hours may lead to saturation. Thermocycling was done, which simulates the changes in temperature in oral environment. Hence in the present study, samples were thermocycled between 5°C, 37°C, 55°C, so as to maintain a difference of 49°C, which approximates the maximum temperature range measured in vivo, as demonstrated by Simmons.^[21] Fluoride ion selective electrode method was used in the present study to measure the amount of fluoride released by the materials, as it is a direct calibration method and it measures total fluoride concentration containing both free fluoride ions and fluoride complexes. Only GICs showed an initial fluoride 'burst' effect in the present study which were in accordance with the results reported by El Mallakh *et al.*,^[9] Suljak *et al.*,^[22] Vermeersch *et al.*,^[24] Attar *et al.*,^[3] while Compomer and Giomer did not show such effect

which were in accordance with study by Attar *et al.*,^[3] Yap *et al.*,^[28] Dhull *et al.*^[6] The burst effect was the initial high amount of fluoride release seen during first 24 hours, which was due to fluoride release from the glass particles as they dissolve in the polyalkenoate acid during the setting reaction while in later days release is slow because of fluoride ability to diffuse through cement pores and fractures as the glass dissolves in storage medium. The two conventional GICs used in this study released statistically different amount of fluoride although both showed initial burst effect during first 24 hours. This could be due to many factors, such as the differences in mixing mechanism, the mixing time, the setting time, the powder: liquid ratio. These results were in accordance with previous studies conducted by Vermeersch *et al.*,^[24] Attar *et al.*^[3] The Glass ionomers released more fluoride with respect to Compomer and Giomer because ion leachable glass is decomposed by proton attack at the surface and subsequently fluoride ion are liberated from glass particle as reported by Vermeersch *et al.*,^[24] Attar *et al.*,^[3] Dionysopoulos *et al.*,^[8] Mousavinasab *et al.*^[18] In the present study, Giomer, released less fluoride than the Compomer in which were contradictory to study done by Itotaa *et al.*,^[13]; Dhull *et al.*,^[6] but it were in accordance with study done by Mousavinasab *et al.*,^[18] who found that there was significant differences in the amount of fluoride release between Compomer and Giomer. This explains that fluoride released by resin based materials, is not only affected by the formation of complex fluoride compounds and their interaction, but also by the type and amount of resin used for the photochemical polymerization reaction. Beautifil (Giomer) showed little amount of fluoride release in this study, which contains surface pre reacted glass ionomer (S-PRG) as a fluoride component. The fluoride glass within Beautifil has little or no glass ionomer matrix phase, because of the lack of any significant acid base reaction. As PRG has been reacted with fluoroaluminosilicate glass and acid, water sorption is not critical in the acid base reaction as seen in this study which were similar to the results of other studies done by Yap *et al.*,^[28] Itotaa *et al.*^[13] Compomers resemble traditional composite resins in that their setting reaction by

polymerization Dyract extra a third generation compomer used in present study showed low diffusion fluoride release. Dyract includes fluoride containing acid degradable glass strontium fluoride and ion leachable glass fillers that are smaller in size than in composites. Its initial setting is performed by light-activated polymerization which is followed by an acid-base reaction that arises from sorption of water into the cement from the surroundings, leading to controlled diffusion of fluoride from the material. The similar findings were reported by Wiegand *et al.*^[25] Difference in fluoride release in different types of Compomers is due to filler systems used in the products. However, the difference in fluoride release between glass ionomers and Compomers is due to the fact that in GICs, fluoroaminosilicate glass particles are the main source of fluoride and they are more soluble and thus release more fluoride. In contrast, the filler particles in compomer and resin composite, typically a mixture of fumed silica, barium aluminofluorosilicate glass, and YbF₃, are usually less soluble than aluminofluorosilicate glass particles in GICs as observed by Xu *et al.*^[27] All materials in the present study showed a steady decrease in release of fluoride with time except glass-ionomer cements where there was significant initial burst release which decreased with time. This pattern of release were also observed in studies done by Eliades *et al.*,^[10] Yap *et al.*,^[28] Asmussen *et al.*,^[2] Itotaa *et al.*^[13] Giomer, have PRG fillers that are already been pre-reacted with polyacrylic acid, so water sorption is not critical in the acid-base reaction process. Fluoride release is via an exchange mechanism in direction of the lowest fluoride concentration. The amount of fluoride release decreases with time due to diminishing gradient, as fluoride is leached out from the material as noticed by Yap *et al.*^[28] This explains the steady decline of fluoride release from Beautifil in the present study over the entire period of the present experiment. For Compomer, the present study was also in agreement with several earlier studies done by Vermeersch *et al.*,^[24] Eliades *et al.*,^[10] that the fluoride release content reduces with time. It may be owing to the formation of a silica gel layer covering the glass particles, thus subsequently declining the fluoride release.

Fluoride containing dental materials usually show clear differences in the fluoride release and uptake characteristics which may act as fluoride reservoir to increase fluoride level in saliva, plaque and hard dental tissues, or may help to prevent or reduce secondary caries. After recharging the specimen with APF gel or NaF gel, the fluoride release from all materials increased substantially after 24 hours (first day). The release did not decline quickly to the baseline level till 72 hours i.e., 3 days since first recharge and thereafter continuous decrease was seen. These results were in accordance with several previous studies Suljak *et al.*,^[22] Rothwell *et al.*,^[20] Preston *et al.*,^[19] where the 'brief burst' effect was reported due to recharged superficial part of the specimens. However, the material with higher initial fluoride release has also shown a higher ability of fluoride recharge in the present study similar to the study done by Xu *et al.*^[27] In present study, exposure to APF gel or NaF gel had equal effects on the amount of fluoride release from all materials except that samples recharged with APF released more fluoride which were in accordance with the studies conducted by Diaz-Arnold *et al.*,^[7] Gao *et al.*^[11] This was probably because of low pH of APF gel containing phosphoric acid and hydrofluoric acid which erodes the surfaces of many restorative materials and contribute to the high release of fluoride and other ions. The permeability of the materials was also likely to be a major factor in the fluoride recharge mechanism. The more permeable material has more ability to absorb and then release fluoride. Resin containing materials are known to have low water permeability or water sorption whereas conventional GIC has been shown to have a greater sorption value. This may explain more fluoride released from GIC when compared to that from Giomer and Compomer in the present study. Moreover, the porosity of the materials may have an influence on the amount of fluoride release before and after recharge. Higher porosity will allow deeper diffusion of the recharge agent into the material and results in a higher content of fluoride storage and release. On the other hand, the material with high porosity has disadvantages on the mechanical properties. An example for this is the material with less resin content, such as conventional and resin-modified GICs. Due to

their higher porosity, they exhibit higher fluoride recharge capabilities. Nevertheless, their strength is lower than that of compomer and resin composite. In addition, the viscosity of fluoride recharge agents may be a factor for fluoride release. The gel viscosity may be difficult to remove from pores and cracks of the specimens by gentle washing as observed by Gao *et al.*^[11] Although Giomers are claimed to be fluoride rechargeable as the pre-reacted surface zone of the glass particles seems to act as a reservoir for fluoride ions the pattern of fluoride re-release did not differ from other materials' patterns. The present study supports the rechargeable behavior of glass-ionomer materials also observed by Cildir and Sandalli,^[4] Debem *et al.*,^[5] in their studies. However, fluoride release after exposure to topical fluoride gels occurred in high amount within 2 days after recharge. In the clinical situation, this would mean that fluoride would be constantly released as long as the subject continues rinsing, brushing, or chewing fluoridated products. The cumulative fluoride release levels of glass-ionomer-based materials after topical fluoride application were generally lower than those released from the freshly prepared specimens after 28th day. This may be expected that the maturity of the cement would affect its fluoride uptake. As the cement ages, the ionic matrix matures and becomes more cross-linked. The required diffusion process would be impeded by the more cross-linked matrix as observed in the present study similar to the finding of Verbeeck *et al.*^[23] The values of liberated fluoride vary substantially from one study to another. This may be attributed to a lack of uniformity in specimen shape and size, process of the experiment, nature of the aqueous environment used, and even the equipment employed to express fluoride release. Hence, although there are lots of studies available in this direction, it is difficult to compare the results from all them.

CONCLUSION

However the present study was in-vitro study where freshly prepared specimens had shown significant variations in fluoride release and recharge potential. This study might not be able to arrive at any conclusive results until compared to in-vivo study conducted with long term follow up. The further investigations are required to

clarify the fluoride recharge mechanism as it is not certain whether the fluoride uptake or recharge properties play any important role in prevention of secondary caries around the restoration.

CONFLICT OF INTEREST & SOURCE OF FUNDING

The author declares that there is no source of funding and there is no conflict of interest among all authors.

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