SUMMARY: The aim of this study was to review the fluoride release and recharge abilities of fluoride-releasing dental restoratives, and discuss the current status concerning the prevention or inhibition of secondary caries. Fluoride-containing dental materials show clear differences in the fluoride release and uptake characteristics. The elution of fluoride is a complex process. It can be affected by several intrinsic variables, such as resin matrix and filler composition. It is also influenced by experimental factors, i.e., storage media, frequency or change of the storage solution, composition and pH value of saliva, dental plaque and pellicle formation. Due to the fact that fluoride levels leached from fluoride containing filling materials decreased over time the “recharging” of restoratives with fluoride has been suggested to maintain a continuously increased level of fluoride release. The ability of a restorative material to act as a fluoride reservoir is mainly dependent on the type and permeability of filling material, on the frequency of fluoride exposure and on the kind and concentration of the fluoridating agent. In vitro, several fluoride-releasing restorative materials have shown to inhibit enamel and dentin demineralization produced by acidic gels or demineralizing buffer solutions. Thereby, inhibition of enamel demineralization is located up to a distance of 7 mm from the edge of the material. Despite the cariostatic effect achieved from an increase of fluoride content in saliva, plaque, and dental hard tissues, clinical studies exhibited conflicting data as to whether or not these materials sufficiently prevent or inhibit secondary caries compared to non-fluoridated restoratives.

Keywords: Fluoride release; Fluoride-releasing restoratives; Fluoride recharge; Inhibition of secondary caries.

INTRODUCTION

The principal reason for restoration failure is secondary caries in both permanent and primary dentition.¹-³ Recommendations have been made to aid in the prevention of secondary caries, including tooth brushing, topical fluoride therapy, sealing restoration margins, and utilization of antimicrobial agents.

Fluoride was introduced into dentistry over 70 years ago, and it is now recognized the main factor responsible for the dramatic decline in caries prevalence that has been observed worldwide.⁴ The effect of fluoride on demineralization and remineralization of incipient caries lesions in enamel and dentin is recognized as the most important mechanism of fluoride action. It has been recognized that the initial carious lesion should be exposed to fluoride in the aqueous phase for a prolonged period of time to achieve the cariostatic effect.⁵⁶

Fluoride present in low, sustained concentrations in the oral fluids during an acidic challenge is able to absorb to the surface of the apatite crystals, inhibiting
demineralization. When the pH is re-established, traces of fluoride in solution will make it highly supersaturated with respect to fluorhydroxyapatite, which will speed up the process of remineralization. The mineral formed under the nucleating action of the partially dissolved minerals will then preferentially include fluoride and exclude carbonate, rendering the enamel more resistant to future acidic challenges. Topical fluoride can also provide antimicrobial action.4

In vitro studies have shown that fluoride released from fluoride-containing restorative materials effectively protected the tooth tissues from demineralization in the region near to the restorative materials.7,8 Fluoride that is in an aqueous phase surrounding dental tissues inhibits demineralization much more effectively than fluoride incorporated into crystals of apatite. Moreover, fluoride precipitated onto tooth surfaces in the form of CaF₂ serves as a reservoir of fluoride when pH drops.

The aim of this study was to review the fluoride release and recharge capabilities of fluoride-releasing dental restoratives, and discuss the current status concerning the prevention or inhibition of secondary caries.

**FLUORIDE-RELEASING RESTORATIVE MATERIALS**

Restorative materials that release fluoride have been noted to effectively inhibit the demineralization of tooth structure adjacent to restorative margins7,8,10-12 (Table).

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Year when first available</th>
<th>Fluoride release</th>
<th>Duration of F release*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional glass ionomer cements (GICs)</td>
<td>Fluoro-alumino-silicate glass (FASG) + polyacrylic acid</td>
<td>1972</td>
<td>High</td>
<td>Until 3 years</td>
</tr>
<tr>
<td>Resin-modified glass ionomer cements (RMGICs)</td>
<td>FASG + polyacrylic acid + resin monomers</td>
<td>1989</td>
<td>High</td>
<td>1–2.7 years</td>
</tr>
<tr>
<td>Polyacid-modified composite resins (Compomers)</td>
<td>Resin monomers + FASG as fillers</td>
<td>1993</td>
<td>Low</td>
<td>Over 3 years</td>
</tr>
<tr>
<td>Composite resins containing PRG fillers (Giomers)</td>
<td>Resin monomers + PRG fillers</td>
<td>1995</td>
<td>Low</td>
<td>Years</td>
</tr>
<tr>
<td>Fluoride-releasing composite resins</td>
<td>Resin monomers + fillers</td>
<td>1985</td>
<td>Very low</td>
<td>Over 5 years</td>
</tr>
</tbody>
</table>

*Data recorded from in vitro studies.*44
Glass ionomer cements have been introduced as fluoride-releasing restorative materials, and they may offer fluoride around restorations.\(^7,13,14\) The disadvantages of these materials, however, include sensitivity to moisture, low initial mechanical properties and inferior translucency compared to resin-based materials.

Hybrid materials combining the technologies of glass ionomers and composite resins were subsequently developed to help overcome the problems of conventional glass ionomer cements (GICs) and maintain their clinical advantages. Examples of these hybrid materials include resin-modified glass ionomer cements (RMGICs) and polyacid-modified composite resins (compomers). These materials have different setting mechanisms. In particularly, RMGICs set by an acid-base reaction and free radical polymerization mechanisms,\(^15,16\) while compomers set by free radical polymerization only with a limited acid-base reaction occurring later as the material absorbs water from the oral environment.\(^15,16\)

Recently, a new category of RMGICs has been introduced for restoration of primary teeth and small cavities in permanent teeth. The major innovation of these materials involves the incorporation of nano-technology, which allows a highly packed filler composition (~69%), of which approximately two-thirds are nano-fillers. Due to these alterations in composition some authors support that these materials belong to a new category of hybrid materials called nano-ionomers.\(^17-19\)

Another category of hybrid materials, which was recently introduced to the dental profession, is known as giomers. Giomers are composite resins, which employ the use of pre-reacted glass ionomer (PRG) technology to form a stable phase of glass ionomer in the restorative. Unlike compomers, fluoro-alumino-silicate glass is reacted with polyacrylic acid prior to inclusion into the urethane resin.\(^20\) Giomers have many attractive features such as fluoride release and recharge abilities, good biocompatibility, smooth surface finish, as well as good esthetics.\(^18,20,21\)

Composite resin restorations are in constantly increasing demand. On the basis of the beneficial effect of the fluoride-releasing glass ionomers, a slow release of small amounts of fluoride from composite resins would therefore be advantageous. Studies of the fluoride-releasing properties of composite resins indicate a long-term release of fluoride, although the amount released is low in comparison with that of the GICs, RMGICs, and compomers.\(^22-24\)

**FLUORIDE RELEASE AND RECHARGE ABILITIES OF RESTORATIVE MATERIALS**

The elution of fluoride is a complex process. It can be affected by several intrinsic and experimental variables, such as resin matrix and filler composition, solubility and porosity of the material, powder-liquid ratio used in preparing the material, method of mixing, amount of exposed surface area of the material, and type of storage media.\(^25-29\)
The mechanism by which GICs release fluoride into an aqueous environment is proposed to comprise two processes. Process I is a short-term reaction which involves rapid dissolution of fluoride from the outer surface into the solution; Process II is more gradual and results in a sustained diffusion of fluoride through the bulk cement. According to previous studies, GICs can release fluoride between 0.5–7 ppm one year after the restorations. Resin-based materials released much lower amounts of fluoride ions than GICs. This may be because they do not undergo an acid/base reaction, or may also be a result of their low initial fluoride content.

It has been reported that GICs can take up fluoride from the environment as a means of replacing fluoride which has been lost. The additional fluoride subsequently can be released into the adjacent tooth structure. The clinical implication of this mechanism may be more significant than the inherent fluoride release of the materials. It has been reported that the recharging ability of GICs is superior to that of composites and giomers whilst fluoride-releasing composite resins have a negligible ability to be recharged with fluoride.

The precise nature of this mechanism is not fully understood, but it has been suggested that the recharging ability in the GICs is dependent on the glass component of the material and in particular upon the structure of the hydrogel layer around glass filler particles following reactions between the glass and polyacid component. The increased fluoride release after fluoride recharge of resin-based restorative materials is most probably because of pores or surface-retained fluoride. Compomers and giomers act more like composite resins than like GICs with respect to fluoride recharge ability, in agreement with previous work.

Generally, the fluoride-recharging ability of a restorative material depends on the composition of the material, on the frequency of fluoride exposure and on the kind and concentration of the fluoridating agent.

**EFFECT OF FLUORIDE-RELEASING RESTORATIVES ON SECONDARY CARIES FORMATION**

Many in vitro studies have shown that fluoride-releasing restorative materials present the ability to inhibit enamel and dentin demineralization produced by acidic gels or demineralizing buffer solutions. This ability depends on the amount of fluoride ions released from the materials. Only restorative materials that release high amounts of fluoride ions such as GICs, have been shown to effectively inhibit the demineralization of tooth structures adjacent to restorative margins. Gjorgievska et al. found that glass-ionomers, both conventional or resin-modified, are more effective at protecting the tooth against further decay than either composites or fluoride-releasing composites, with the best protection of all being provided by conventional glass-ionomers. The nature of the tooth had no influence on these outcomes.
Inhibition of enamel demineralization is shown to occur in vitro to a distance of even 7 mm away from RMGIC restorations. Tantbirojn et al. found that under an in vitro demineralization challenge, glass-ionomer liners in an open-sandwich restoration exhibited pronounced inhibition zones at the dentin margin and lowered the amount of mineral loss in the vicinity of 0.25 mm from the restoration interface. Another study reported that the degree of protection was highest in the closest vicinity of the restorations and the depth of lesions increased with the distance in an inverse relationship to fluoride released.

Mohammed et al. investigated the mechanistic action of fluoride on inhibition of enamel demineralization using $^{19}$F magic angle spinning nuclear magnetic resonance (MAS-NMR). At and below 45 ppm F$^-$ in the solution, $^{19}$F MAS-NMR showed fluoride-substituted apatite formation, and above this fluoride concentration, CaF$_2$ formed in increasing proportions. Further increases in F$^-$ caused no further reduction in demineralization, but increased the proportion of CaF$_2$ formed. The presence of 43 ppm Sr$^{+2}$ in addition to 45 ppm F$^-$ increases the fraction of fluoride-substituted apatite, but delays formation of CaF$_2$ when compared to the demineralization of enamel in fluoride-only solution.

It has been found that the reduction of lesion depth of conventional GICs compared to non-fluoridated materials ranged from 58% to 80%. Likewise, for RMGICs the reduction of lesion depth ranged from 35% to 75%, while for fluoride-releasing composite resins ranged from 9% to 40%.

It has been assumed that GICs may present complete inhibition of demineralization around restorations. This evidence has been reported previously and was attributed to the high fluoride release from GICs. Dijkman et al. reported that a monthly cumulative fluoride release of 200–300 µg/cm$^2$ is sufficient to completely inhibit enamel demineralization. Jacobson et al. showed that a concentration of fluoride ions of approximately 3 ppm initiates the remineralization of enamel, while at lower concentrations there is no inhibition of demineralization of enamel. Furthermore, it has been reported that fluoride concentrations of between 5 and 80 ppm at the interface between restoration and tooth tissues may be the optimal range to prevent caries formation.

Most in vitro studies have found evidence for inhibition of enamel demineralization surrounding restorations by fluoride-releasing restoratives, although they were not able to eliminate the enamel lesions. Currently, relatively few in vivo and in situ studies investigated the demineralization behavior of enamel adjacent to fluoride-releasing restorative materials. The results of these studies are not consistent, thus the clinical relevance of fluoride-releasing restoratives is still debatable. Some in vivo studies found association of fluoride release from restorative materials with inhibition of secondary caries formation around restorations but some others did not find any relation.

In oral environment the caries protective effect of fluoride-releasing materials may be related to the material’s ability to release adequate amounts of fluoride
ions for sustained periods of time and during acidic attack. Fluoride recharging ability of the materials, utilizing fluoridated agents, such as fluoride solutions, gels or dentifrices, may be of great importance for this purpose.

CONCLUSIONS

In conclusion, fluoride-releasing restorative materials reduce enamel and dentin demineralization around restorations but in different extent, depending on their fluoride release ability. Glass ionomer materials exhibit greater effectiveness on inhibition of dental tissues demineralization than resin-based materials. Fluoride-releasing restoratives may be useful as a part of a caries preventive program, especially for patients with high caries risk. Further clinical studies, preferably in split-mouth design, are needed to evaluate the impact of fluoride-releasing restoratives on secondary caries formation.

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Dionysopoulos


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