

FLUORIDE RELEASE AND UPTAKE PROFILES OF GLASS IONOMER CONTAINING RESTORATIVES

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Summary

Glass ionomer cements (GIC) and their derivatives are known for their fluoride releasing properties. These materials not only releases fluoride but can also take up fluoride from the surroundings and re-release it. Many formulations of glass ionomer are being developed to improve their properties and widen their clinical applications. Newer GIC containing materials including highly viscous glass ionomer (HVGIC) and Giomer (PRG Composite) have yet to be systematically investigated.

A wide range of glass ionomer containing materials including HVGIC, resin modified glass ionomer (RMGIC) and composites were investigated in this study. In this project, the effect of maturation time on the fluoride release and surface roughness was studied. As the oral cavity is subjected to various intrinsic and extrinsic chemical challenges, the effect of acidic environment was also investigated. Lastly the recharge ability of the materials using various immersion mediums was investigated to predict their longer term fluoride release.

Results from the study suggest that both fluoride release and surface roughness increase when glass ionomer containing materials are exposed to early moisture and low pH. The amount of fluoride release was dependent on the material type. The inclusion of resin in the material's chemistry makes them more resistant to a harsh chemical environment. Giomer showed better resistance to degradation in low pH compared to HVGIC and RMGIC. When recharging was performed, HVGIC showed

the highest recharge potential whilst Giomer showed the least. More fluoride is released by early exposure to moisture and low pH by HVGIC at the expense of increased surface roughness. HVGIC is the material of choice if high fluoride release is desired clinically.

Notice

Sections of these results and related research have been presented in a conference.

Conference Paper

1. S. Ahmed, AUJ.Yap, JCL. Neo and HC. Ngo. Effect of environmental pH on glass ionomer containing restoratives. 24th IADR-SEA Annual Scientific Meeting, Sept 2010, Taiwan.

Chapter1: Introduction

Dental caries is one of the most common oral diseases. If left untreated, it can lead to the early loss of dentition in both children and adults (Beltran-Aguilar *et al.*, 2005). With the introduction of fluoride and better dental hygienic measures, a decline in caries incidence has been observed in developing countries. This decline is, however, restricted to coronal caries. The incidence of root caries in the adult population has increased due to gingival recession and that people keep their teeth longer (Griffin *et al.*, 2004). Recurrent caries other than bulk fracture is one of the main reasons of replacing a restoration.

When restoring a decayed tooth, a more surgical approach of removing the entire infected as well as sometimes affected structure and subsequently filling it with a suitable material had traditionally been taken. In more recent years, Restorative Dentistry has taken a new direction and emphasis has been placed on maximum conservation of tooth structure. For scientists and dentists, conservation and prevention of tooth structure from caries attack has become a desirable goal. The traditional method of “Extension for Prevention” by G.V Black has been replaced by Minimal Invasive Dentistry techniques (MID). One approach in MID is the atraumatic restorative treatment (ART) which was developed for countries for which conventional methods are not practical.

In addition to several other measures, numerous research have been undertaken to develop a restorative material that not only fulfils the functional and aesthetic demands but should also be able to remineralise the surrounding tooth structure. Among the several tooth coloured restoratives, Glass ionomer cement (GIC) is unique

due to the presence of fluoride as part of its chemistry, which is a key element in remineralisation and preventing demineralization of tooth structure. The chemical and biological role of these cements in caries prevention has widely been attributed to its fluoride releasing capability. GIC has been assigned the principal restorative material for ART, possessing the ability to remineralise the affected dentine left at the base of the restored cavity (Ngo *et al.*, 2006). Not only remineralisation of the affected dentine but also reduction of cariogenic bacteria was found clinically after the removal of the glass ionomer fillings (Duque *et al.*, 2009; Massara *et al.*, 2002).

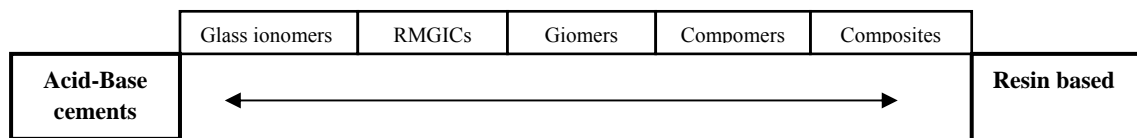


Fig1.1: Tooth coloured restoratives follows a continuum based on their setting chemistry

Tooth coloured materials follow a continuum from acid-base glass ionomer cement to resin based composites (**Fig 1.1**). Glass ionomers and resin-based composites have their own individual disadvantages and advantages. In order to optimize their properties, several modifications were done. Adding resin component to glass ionomer produced resin modified glass ionomer cements (RMGIC), which were developed to control the early moisture sensitivity of GIC meanwhile retaining its ion exchange remineralisation phenomenon (Mount *et al.*, 2009). Similarly, attempts have also been made to add glass ionomer components to composite resins for fluoride release. To improve the mechanical properties, polyacid modified composite resin (compomers) were developed which was also capable of fluoride release and recharge. Giomers, another hybrid which comprises of pre-reacted glass ionomer

fillers added in resin base, resulted in better aesthetics, polishability and handling characteristics. GIC and their derivatives have not only shown the property of long term fluoride release but also possess the potential to take up fluoride from the surrounding acting as a fluoride reservoir and re-releasing the fluoride for further caries inhibition.

The application of these materials depends on the clinical situation. As the oral cavity is exposed to various chemical and biological changes, a material with better longevity and a potential fluoride reservoir is desirable in the oral environment. Similarly, clinical situations where hyposalivation prevails either due to radiation or xerostomia, chemical and biological changes take place in the oral cavity which increases the risk of caries and/or secondary caries. Glass ionomer containing materials have been shown to reduce the incidence of secondary caries in the xerostomic patient. However, the structural integrity was better maintained in composite resins than GIC (De Moor *et al.*, 2009).

All the restorative materials in the mouth are subjected to degradation. GIC due to its polysalt matrix is more prone to disintegration. Many studies have been done to explore the properties of glass ionomer containing cements to achieve the maximum benefit. Many new materials are being introduced and the gap of knowledge needs to be filled. Giomer, the newest addition in the continuum of aesthetic materials, requires investigation as limited studies have been conducted on it. Similarly Highly viscous glass ionomer (HVGIC) also demands further investigation due to its growing demand for ART. Glass ionomer containing materials are exposed to various changes in the mouth which can affect their longevity and directly or indirectly affects the amount of fluoride release. The purpose of this study is to investigate the fluoride

release profiles and surface integrity of commercially available glass ionomer containing materials with respect to various environmental changes and to predict their fluoride reservoir potential.

Chapter 2: Literature Review

2.1: Dental caries

Dental caries is a transmissible disease caused by the bacterial fermentation of carbohydrates, producing acids which causes dissolution of the dental hard tissues (Featherstone, 2008). There are several pathological factors involved in the dissolution or demineralization of tooth structure. These pathological factors include cariogenic bacteria, substrate (carbohydrates) and salivary dysfunction (Featherstone, 2000). Nature has provided numerous protective factors to balance these pathological factors. The disease only leads to cavitation when there is an imbalance between the pathological and protective factors (**Fig 1.2**)

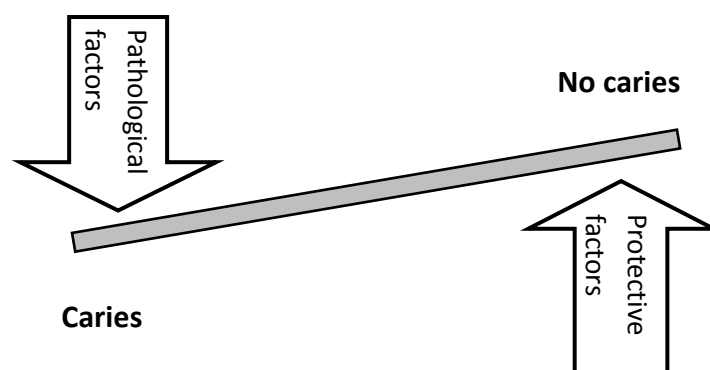


Fig 1.2: The imbalance between the protective and pathological factors leads to the caries process (adapted from Featherstone *et al.*, 2009)

The process of dental caries is a combination of biological, chemical and physical events. Oral cavity has a diverse microbial ecology and all the hard surfaces in the mouth are susceptible to microbial attachment. The initial attachment of early colonizers, later followed by secondary colonizer subsequently leads to the formation of biofilm on the tooth surface. The metabolically active biofilms ferment carbohydrates and produce organic acids as a by product (Featherstone, 2000). The bacteria have to be acidogenic (able to produce acids) and acidouric (able to survive in acidic environment) to be considered as pathogenic (Garcia-Godoy and Hicks, 2008). Although many bacteria are present, mutans streptococci and lactobacilli are considered as the chief pathogens of dental caries (Featherstone, 2000; Garcia-Godoy and Hicks, 2008). This postulation is debatable, since these organisms are rather indicative of the environmental condition than being considered as the causative factors (Fejerskov, 1997). There has been no direct association of caries with these species, as caries can also occur in their absence and there could be no sign of caries in the presence of mutans streptococci (Marsh, 2006).

Saliva directly and indirectly helps in maintaining oral homeostasis and the integrity of tooth structure (Hicks *et al.*, 2004). It acts as a vehicle and carries many protective factors that are essential to reverse the process of demineralization and re-deposits the lost minerals i.e. remineralisation. These factors include calcium, phosphate and fluoride required for the reformation of the acid attacked crystal structure. It also contains acid buffering components and antibacterial agents (Garcia-Godoy and Hicks, 2008). It is worth mentioning that saliva is not always in direct contact with the tooth surface and an interface is usually present i.e. biofilm or the plaque. The acids produced as the by product of carbohydrate metabolism tend to bring a shift in

the resting pH of the biofilm and it decreases from 7.0 to 5.5, which is the critical pH of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}_2$ (Garcia-Godoy and Hicks, 2008). The critical pH occurs when the overlying fluid is just saturated with respect to the hydroxyapatite crystals. Further decrease in pH causes the dissolution of crystals and induces demineralization. The H^+ ions attack the crystal lattice and form complexes with PO_4^{3-} and OH^- , thus making the fluid undersaturated and act as a driving force for more ions to leach out (ten Cate, 2003). Although the structure and chemical composition of enamel do affect the kinetics of demineralization, diffusion was considered as the rate-limiting step (Robinson *et al.*, 2000).

The normal physiological level of calcium, phosphate and fluoride is higher in the overlying plaque than saliva (Hicks *et al.*, 2004). After the acid attack, plaque fluid becomes understaturated with respect to hydroxyapatite and a subsurface lesion forms. The surface layers, however, remain intact as the fluid remain supersaturated with respect to fluorohydroxyapatite (ten Cate, 2003). The supersaturated fluid allows the process of reprecipitation on partially damaged crystals. The reprecipitation also occludes the possible ingress of ions in the body of the lesion and leaves an intact surface with a subsurface lesion, clinically diagnosed as 'white spot' lesion (Featherstone, 1999; Garcia-Godoy and Hicks, 2008). Therefore a low and constant supply of the calcium, phosphate and fluoride ions are required for effective remineralisation to take place (Hicks *et al.*, 2004).

2.1.1: Fluoride and Dental caries

Fluoride does not have a direct role in preventing caries. The advent of fluoride in dentistry has been a major landmark in reducing caries incidence. The role of fluoride in preventive dentistry was established nearly 60 years ago. Fluoride was thought to reduce enamel solubility by its incorporation into the lattice structure in the pre-eruptive stages of tooth development. This, however, was found to be untrue (Castioni *et al.*, 1998). The simultaneous dissolution of tooth structure allows the incorporation of fluoride ions in the post eruptive stages of tooth development (Fejerskov *et al.*, 1994). Fluoride not only inhibits caries but also halts the process of caries progression in many ways. The presence of fluoride in the surrounding medium inhibits demineralization and promotes remineralisation by reconstructing partially damaged hydroxyapatite crystal structure. This forms a structure which is less susceptible to acid attacks. Fluoride was also found to be antibacterial, reducing the overlying plaque microorganisms (Featherstone, 1999).

2.1.1.1: Fluoride - role in demineralisation and remineralisation

Dental hard tissues principally composed of inorganic compound closely resemble calcium hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ which has a defined structure. Although the biological apatites resembles the pure calcium hydroxyapatites but still differs in stoichiometry, composition and morphology. Dental apatite is essentially a carbonated apatite, their imperfect crystalline structure allows substitution of many ions and thus changes the solubility product (K_{sp}) of the apatite (ten Cate and Featherstone, 1991). The inclusion of carbonate and magnesium induces instability. The presence of

fluoride improves the crystallinity of the structure (Robinson, 2009). Fluoride competes for hydroxyl ions in hydroxyapatite structure and can either form fluoroapatite or fluorohydroxyapatite, the latter is of which more likely to form in human enamel. The resulting F-replaced hydroxyapatite has a lower solubility product which is due to its high charge density and its symmetry, moreover reduces the lattice energy and stabilizes the crystal structure (Robinson *et al.*, 2000). XRD (X-ray diffraction spectroscopy) has shown that inclusion of fluoride or other trace metals in carbonated apatite resulted in a much better crystalline structure than pure carbonated apatite (Featherstone and Nelson, 1980). The pre-eruption absorption of fluoride from the tissue fluids and the post eruption inclusion of fluoride from saliva contribute to a higher amount of fluoride in the superficial layer of enamel than the deeper layers (Robinson *et al.*, 2000). The presence of fluoride in the solution surrounding the crystals has been found to be more effective in inhibiting demineralization as it travels along with acid and is absorbed on the crystal surface and prevents dissolution of crystals (Featherstone, 2000; 2008; Garcia-Godoy and Hicks, 2008). This process is rather associated with decrease in demineralization than remineralisation as the structure formed is different than the one being replaced (Cury and Tenuta, 2009).

Fluoride has a very integral role in maintaining the balance between demineralisation and remineralisation. After the source i.e. carbohydrates is depleted and saliva neutralizes the acids, the pH of the plaque is restored back to the resting pH. The deficient crystals act as nucleates and attract calcium and phosphate and along with fluoride forms fluoro-hydroxyapatite, which is less susceptible to acid attack compared to carbonated hydroxyapatite (Cury and Tenuta, 2008; Featherstone, 2008). Thus for remineralisation to take place the presence of calcium, phosphate and

fluoride is essential (Featherstone, 2009). The shift from demineralization to remineralisation is possible only if the overlying biofilm fluid or the saliva becomes supersaturated with respect to hydroxyapatite. In some studies, a constant low supply of fluoride is recommended for effective remineralisation (Garcia-Godoy and Hicks, 2008; ten Cate and Featherstone, 1991). Conversely a high clinical dosage of fluoride was favoured as the postulation is that the mineral gain in artificial lesions was found to be dose dependent and likelihood of fluoride surrounding the crystals increases (Hellwig and Lussi, 2001).

2.1.1.2: Antibacterial Properties of fluoride

Numerous studies have established the antimicrobial activity of fluorides. However, its anticariogenic property still remains debatable since most of the studies supporting the arguments were performed. Fluoride works in two main ways (1) inhibiting a wide variety of enzymes (Koo, 2008) and (2) enhancing the proton permeability of cell membranes by forming hydrofluoric acid (HF) which discharges Δ pH across the membrane, and causes acidification of cytoplasm and inhibition of glycolytic enzymes (Koo, 2008).

Secondary caries has been identified as the one of the major reasons for replacing existing restorations (Forss and Widstrom, 2004; Mjor *et al.*, 2000). The formation of bacterial biofilms on all the hard surfaces of the mouth is inevitable. Therefore the need of preventing or minimizing the formation of cariogenic biofilm is also one of the requirements of an ideal restorative material. Several studies have suggested the antibacterial activity of fluoride releasing materials (Benderli *et al.*, 1997; Forss *et al.*,

1991; Friedl *et al.*, 1997; Hengtrakool *et al.*, 2006). It has been postulated that GIC either inhibits the bacterial growth or prevents adherence by an initial outburst of fluoride release and initial low pH of the cement (Vermeersch *et al.*, 2005). The high fluoride content of plaque covering ionomeric material was considered responsible for the reduction of enamel demineralisation by interfering with the bacterial metabolism (Tenuta *et al.*, 2005). The antibacterial property was mainly contributed by the fluoride release, although in a few studies the complementary role of other ions has also been highlighted (Hengtrakool *et al.*, 2006). The percentage of *S.Mutans* collected from the overlying plaque of restorations from a group of children was found more to be extensive for composites and amalgam than glass ionomer cements (Svanberg *et al.*, 1990). A high fluoride uptake in the enamel and low mutans count on GIC restorations was observed in an in situ study (Benelli *et al.*, 1993).

The antibacterial activity of GIC is highly debatable as many studies completely nullify the antibacterial aspect of GIC (Eick *et al.*, 2004; Palenik *et al.*, 1992). One of the studies suggested the action of fluoride to be insignificant in reducing or inhibiting the bacterial growth as the biofilm growth was found to be more dominant on the surfaces of GIC compared with other materials (Al-Naimi *et al.*, 2008). The antibacterial effect of GIC needs further elucidation. So far the studies have just been able to determine the short term antibacterial potential of GIC and the responsible factors could most likely be the acidity of the initial set or the initial outburst of fluoride release. However, clinically long term antibacterial effect of GIC is desirable. Details of the exact mechanism of bacterial inhibition are still unknown and studies need to be done to further validate the anticariogenic potential of this cement.

2.2: Fluoride and Restorative materials

The oral cavity acts as a reservoir for fluoride and to maintain a cariostatic environment, a constant supply of topical fluoride is vital (Castioni *et al.*, 1998). In recent years, due to the therapeutic effect of fluoride, many oral health care products have been introduced in the market incorporating fluoride as their major constituent. Restorative dentistry is no exception, the idea of restoring a tooth with added caries prevention has led to the inclusion of fluoride into dental restoratives either as part of the chemistry or as additive. Fluoride was first used as the main constituent of the glass component of dental silicate cements. However, due to poor physical and mechanical properties this material was later replaced by glass ionomer cements. The beneficial aspects of glass ionomer are well recognized. It chemically adheres to tooth structure and releases and uptakes fluoride on a continuous basis.

Inferior mechanical strength is the main drawback of GICs and to broaden its application, several modifications have been developed. In some of these materials, the parent compound and chemistry has remained the same, with some modifications which resulted in the resin modified glass ionomer cement, polyacid modified composites and giomers. Attempts have also been made to incorporate fluoride in composites and amalgam. However, fluoride release from these materials gradually decreases with time. GICs are believed to possess the recharge capability affording the long term protection against cariogenic attacks.

2.3: Glass ionomer containing restorative materials

2.3.1: Glass ionomer cements

Glass ionomer was discovered to overcome the drawbacks of silicate cements. Alan Wilson and Brian Kent altered the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in silicate glass and developed the material which was initially named as ASPA, aluminosilicate polyacrylate cement (Wilson and Kent, 1972). This tooth coloured restorative was defined by Crowley *et al* (2007) as an acid-based cement formed by reacting a polycarboxylate (e.g. poly acrylic acid or acrylic/maleic acid copolymer) with an ion-leachable acid degradable glass of the generic form $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-XF}_2$ (X being any bivalent cation) in the presence of water to produce a cross linked hydrogel matrix in which the glass-filler phase is embedded (Crowley *et al.*, 2007).

2.3.1.1: Composition and Setting Chemistry

Since its advent, glass ionomer cement has undergone many changes. However, the basic chemistry has remained the same. The cement basically consists of ion leachable glass particles and polyalkenoic acid and the two components react in the presence of water to yield set cement (Fig 1.3). The glass formulations which have been widely studied are $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2$ (Nicholson, 1998).

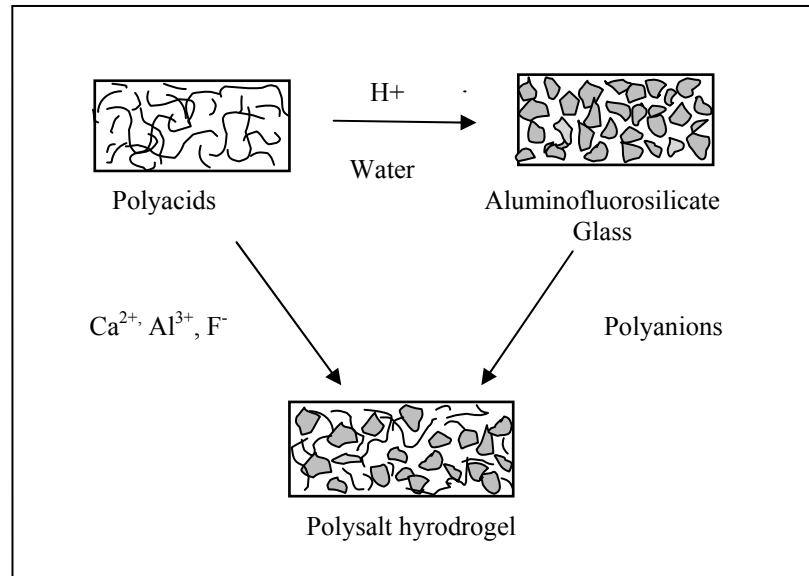


Fig1.3: Reaction of polyacrylic acid with glass particles results in formation of Polysalt hydrogel (set cement).

The glass particles are prepared by fusing alumina, silica, metal oxides and metal fluorides at a very high temperature usually ranging from 1200-1550⁰C .To give cement its radiopacity, barium, lanthanum and strontium are also added. The molten mixture is shocked cooled and are grounded to fine particles, the size of which varies according to the clinical usage of the cement (Nicolson 1998). Fluorine and phosphates are added to the glass composition as they tend to reduce the melting temperatures and enable the material to have better working/setting characteristics. Fluoride act as a flux and facilitates the breaking of the glass network to make the acid attack easier (Griffin and Hill, 2000). Clinically, fluoride lowers the refractive index, allowing for more aesthetics which are useful for anterior restorations and also provides anti-cariogenicity to the material (Griffin and Hill, 2000).

Polyacrylic acid is another essential component of glass ionomer cements. Initially 45% polyacrylic acids were used but were soon discarded due to early gelation and a reduced shelf life. Several variations of polyacrylic acids either as homopolymers and/or its co-polymers like itaconic acid, maleic acid, di- or tri carboxylic acid were introduced to overcome the problems of gelation (Smith, 1998). Water is an indispensable component of glass ionomer cement. The acid-base reaction requires an aqueous medium for the initiation of the setting process. Water breaks the internal hydrogen bonding for acidic carboxylic groups and facilitates their reaction with glass particles (Hickel *et al.*, 1998). Tartaric acid is also added to the cement formulation as a rate controlling additive. Being a stronger acid, it reacts with the glass particles and forms stable metal ion complexes which allows an increase in the working time and a reduction in the setting time (Smith, 1998).

The setting of glass ionomer cement is initiated as soon as the acid reacts with basic glass particles in the presence of water leading to the formation of polysalts. However, the reaction is not as simple and it can be divided into three stages. The first stage involves dissolution in which the protons from acid react with the outer surface of glass particles. This causes the leaching of many non-network and network forming ions which are mainly Ca^{+2} and Al^{+3} . Tartaric acid at this stage reacts with glass and prevents the premature formation of Ca-acrylate salts thus prolonging the working time. The preferential sites for acid attack are usually the Ca rich ones as they are believed to be more basic in nature (Nicholson, 1998).

Dissolution is followed by gelation. This initial setting takes place due to weak ionic cross linking between the carboxyl groups and released Ca and Al ions, which also contributes to the viscoelastic behaviour of the freshly set material (Smith, 1998). In the last phase of hardening, the formation of Al-polyacrylates supercede the Ca-acrylate salts and enables the material to acquire strength and rigidity. The material gains its final strength after 24-48 hours which may continue for several months.

2.3.2: Resin modified glass ionomer

Resin modified glass ionomer cements (RMGIC) were developed to control the early moisture sensitivity of conventional glass ionomer cements. Resin modified materials share the chemistry between conventional glass ionomer cements and composites as the material is modified by resin and at the same time it retains the characteristics of GIC (McCabe, 1998). It contains a resin component from composite resin and ion leachable glass from GIC to optimize the useful properties of the two materials. RMGICs have been able to overcome the problem of moisture sensitivity and are believed to have better aesthetics and strength than conventional GICs (Smith, 1998). RMGICs also share the fluoride release/uptake and chemical adhesion characteristics of conventional GICs. However, resin addition makes it prone to polymerization shrinkage.

2.3.2.1: Composition and Setting Chemistry

The basic components are similar to conventional glass ionomer i.e. fluoroaluminosilicate glass, polyacrylic acid and water. However, it contains an

additional resin component, 2-Hydroxyethyl Methacrylate (HEMA) (Percq *et al.*, 2008). Different methods have been employed for the production of RMGICs. The interpenetrating network of resin matrix with GIC matrix is achieved just by simply adding up the two components along with the photoinitiators. In the other method, polyacid is modified partially by attaching a polymerizable group (Guggenberger *et al.*, 1998). RMGICs are light activated materials, whilst still retaining the acid base reaction which remains an integral part of its setting chemistry (Burke *et al.*, 2006). The light activated polymerization predominates the setting mechanism of RMGICs, whereas the acid-base reaction starts after 4 days of mixing (Wan *et al.*, 1999). The acid base reaction starts as soon the material is mixed or being sensitive to ambient light, the polymerization can be initiated with dental operating lights and this explains the short working time of these materials (McCabe, 1998).

2.3.3: Polyacid modified composites / compomer

The word “Compomer” was derived from composites and glass ionomer, since its chemistry shares a close proximity with composites. Hence, “polyacid modified composites” is a more apt term for these materials (Guggenberger *et al.*, 1998). The material is available as a single paste system as the mixing time has been eliminated and requires a primer for its bonding.

2.3.3.1: Composition and Setting Chemistry

The material primarily contains all the components of composite resin. In addition, it contains dimethacrylate monomer with carboxylic groups and strontium

fluorosilicate glass (Hickel *et al.*, 1998). It completely sets by polymerization as with composite resin. However, a limited acid base reaction is expected to occur at the later stage (McCabe, 1998). Unlike RMGIC, the water component is completely absent from polyacid modified composites. The dimethylacrylate with carboxylic acid groups makes the setting chemistry more unique as the material can undergo polymerization with methylacrylate terminated resin and the acid-base reaction can take place with the presence of carboxylic groups, water and metal ions (Zimehl and Hannig, 2000).

2.3.4: Pre-reacted Glass ionomer Composites (Giomer)

In vitro studies have reported the fluoride release, recharging and cariostatic capability of PRGs (Okuyama *et al.*, 2006a; Okuyama *et al.*, 2006b; Yap *et al.*, 2002). The fluoride releasing ability of Giomer was found to be more than that of compomers (Yap *et al.*, 2002). The material offers good colour matching, less marginal leakage, and the siliceous hydrogel contributes to high fluoride release among its contemporary resin based materials (Matis *et al.*, 2004). The ligand exchanges within the hydrogel layer is responsible for sustained fluoride release and does not affect the filler-matrix interface unlike compomers (Tay *et al.*, 2001). Being a resin based material, it requires light activation and bonding agent for adhesion. The material is fairly new among the other tooth coloured restoratives, and consequently limited literature is available on giomer.

2.3.4.1: Composition and Setting Chemistry

Giomer is a relatively newer material among the tooth coloured restoratives and contains a unique component of pre-reacted glass ionomer particles (PRG). This material is a hybrid of glass ionomer and composite resin. In this technology the glass particles are reacted with polyacid in an aqueous medium to produce siliceous hydrogel, which is freeze dried, ground milled and silanized to produce PRGs (Ikemura *et al.*, 2003). The resin matrix consists of hydroxyethyl methacrylate (HEMA) and urethane dimethylacrylate (UEDMA). The polyacid is completely eliminated as the particles have already been reacted. Hence, water sorption is not crucial for the initiation of an acid base reaction (Yap *et al.*, 2002). Giomers are further divided based on fully reacted glass particles (F-PRG) and surface reacted particles (S-PRG).

2.4: Fluoride release of Glass ionomer containing materials

GIC has the unique intrinsic property of releasing fluoride, which was added initially in the glass component to act as flux. In the past, several studies have been focused on the fluoride releasing mechanism, mainly due to its cariostatic effect. It releases many organic and inorganic compounds depending on the composition of the parent compound and the released ions are structurally insignificant to the matrix. Hence, their removal does not clinically deteriorate the cement (Crisp *et al.*, 1980b). The conventional glass ionomer releases several ions including fluoride, calcium, aluminium, sodium and phosphate over a long period of time (Kuhn and Wilson, 1985). The association of fluoride with the inhibition of secondary caries was first

observed in the silicate cements. Glass ionomer was mainly introduced to overcome the drawbacks of silicate cements and the fluoride release was found similar to silicate cement over the period of 12 months (Swartz *et al.*, 1984).

Several *in vitro* studies have been done to elucidate the mechanism of fluoride release from glass ionomer cement (Forsten, 1990; Swartz *et al.*, 1984; Wilson *et al.*, 1985). The comparison of fluoride release pattern among several studies and its mechanism is extremely difficult to elucidate as till now there is no standard way of analyzing it. The fluoride release profile observed in most studies showed the similar trend i.e. an initial outburst lasting up to 24-48 hrs with a follow up of a gradual release of fluoride (DeSchepper *et al.*, 1991; Forsten, 1990). In the initial 24 hours, the glass particles readily react with the polyacrylic acid and releases fluoride ions. An early exposure of water or saliva renders its dissolution which results in the initial 'outburst' phenomenon. Hence, it was postulated that the initial "outburst" is due to initial surface dissolution whereas the gradual release is due to the diffusion of ions through the bulk of the cement (Wiegand *et al.*, 2007). It was also observed that in the initial 24 hours the percentage of fluoride released ranges between 52-85% of the total cumulative amount of fluoride released for three months (Vermeersch *et al.*, 2001).

Kuhn and Wilson (1985) proposed that the ion release mechanisms are surface wash off, diffusion through pores and cracks and diffusion through bulk. The ionic release is a diffusion based phenomenon. The cumulative release of fluoride is proportional to the square root of time (Mitra, 1991; Tay and Braden, 1988). Different equations have been proposed in various studies to represent the time dependent fluoride release and follows Fickian's law of diffusion.

- 1: $[F]_t = a + b\sqrt{t} + ct$ (Kuhn and Wilson, 1985)
- 2: $[F]_t = [F]_i(1 - e^{-bt}) + \beta\sqrt{t}$ (Tay and Braden, 1988)
- 3: $[F]_t = \frac{[F]_i t}{\left(\frac{t}{2} + t\right)} = \alpha t$ (Verbeeck *et al.*, 1998)

2.4.1: Factors influencing fluoride release

The mechanism of ionic release is not as simple as it seems to be. *In vitro* tests cannot simulate the oral environment. In the mouth, chemical, physical and biological factors contribute to the dissolution of restoration. Most of the *in vitro* studies for fluoride release were performed in deionized water, artificial saliva or pH solution of varying strength. As different parameters have been employed in previous studies, comparisons are extremely difficult. In GICs, glass particles provide all the network and non-network forming ions. It can be expected that the total fluoride content and the reactivity of glass particles dictate the amount of fluoride released by the cement (De Maeyer *et al.*, 1999). However, there are many intrinsic as well as extrinsic factors which are responsible for the variations of the ionic release from glass ionomer cement. The extrinsic variables can also alter or mask the effect of intrinsic variables (De Moor *et al.*, 1996). The intrinsic properties of the material are also manufacture dependent and the exact composition of cement is never revealed.

De Moor *et al* studied the effect of the intrinsic variables on the quantitative and qualitative assessment of fluoride release. Comparison of the same product from the same manufacturer but using different manipulation methods (hand mix and encapsulated) showed variation in the initial fluoride release. Based on numerous

studies, it has been established that the release of ions which is dissolution- diffusion based is similarly dependent on the exposed surface area of the material. The formulations of GIC also govern the exposure of surface area to saliva. In Miracle Mix where the amalgam is not chemically bonded to the matrix, the release of F^- was due to an increased surface area, whereas in Ketac Silver, the release was less as the particles are sintered with glass, creating a chemical bond to the matrix preventing the ingress of saliva. An increase in microporosity in turn increases the surface area which is responsible for the high F^- release (DeSchepper *et al.*, 1991). Intrinsic variables which could be physical as well as chemical can have an effect on the fluoride release.

The oral cavity is a highly dynamic environment and is exposed to conditions that influence the stability of dental restoratives. In *in vitro* studies the stability and performance of the materials are dependent on many factors and are not similar to the *in vivo* situations. The temperature in the mouth is never steady; it keeps changing with dietary intake. The release of F^- was also studied with respect to temperature changes and the release was found to increase by raising the temperature of the eluting medium (Yan *et al.*, 2007). The ionic release of glass ionomer has been studied in different mediums but in most of these studies, deionised water was used as the eluting medium. Artificial saliva has also been studied to simulate the oral conditions (DeSchepper *et al.*, 1991). The composition of artificial saliva is close to human saliva, yet it does not completely simulate the human saliva's composition. The fluoride release was found to be continuous but of lesser magnitude in human saliva than in artificial saliva implying that many biological and chemical factors in the oral cavity can reduce the ionic release (Hattab *et al.*, 1991). The findings were

consistent when human saliva was used as an immersion medium, suggesting that the salivary pellicle could retard the ionic diffusion (Bell *et al.*, 1999).

Various studies have also been done to evaluate the stability and the fluoride release of the glass ionomer under different acidic condition simulating the oral environment with its various pH conditions contributed mainly by diet and cariogenic challenges. Acidic pH was responsible for the increase in fluoride release and these findings were similar in many studies using pH as a variable (Carey *et al.*, 2003; Carvalho and Cury, 1999; Silva *et al.*, 2007). Consequently, it was postulated that elevated fluoride release in acidic pH contributes to the dissolution phenomenon of glass ionomer cement.

2.4.2: Methods of assessing fluoride release

Fluoride, either from environmental or biological samples can be detected by numerous methods. The extensive methods employed in fluoride detection are beyond the scope of this literature review, only the techniques used in dentistry for the detection of liquid samples will be discussed.

Fluoride in biological samples exist as inorganic form which can be further divided into ionic (uncomplexed fluoride) and non-ionic (complexed fluoride) forms (Venkateswarlu, 1994). Fluoride is usually present in biological fluids at trace levels and care should be taken to use a technique which offers lower detection limits and sensitivity for precision and accuracy. The techniques used in dentistry included potentiometry (Ion Selective electrode) and chromatography (Ion and Gas chromatography).

The potentiometric method or ion selective electrode (ISE) is widely used in dentistry for fluoride detection (Forsten, 1994; Hatibovic-Kofman *et al.*, 1997; Swartz *et al.*, 1984). It consists of a probe or electrode which is selective for each ion to be analyzed, a meter and a buffer (Total Ionic Strength Adjustment Buffer, TISAB). The buffer is to be mixed with the samples and its function is to decomplex the ions, provide a constant background and balance the pH. ISE offers many advantages over other methods, including low cost, ease of use and accuracy. The minimum detection limit of ISE is 0.02 ppm.

Ion chromatography (IC) is another method used in dentistry for fluoride detection (Itota *et al.*, 2004; McCabe *et al.*, 2002; Yap *et al.*, 1999). This method is expensive, time consuming and technique sensitive. However, it offers lower detection limits, better accuracy and precision. IC enables the measurement of fluoride at ultra trace levels i.e. ppb whereas ISE's minimum detection limits is at ppm level. IC also allows the detection of free fluoride whilst ISE enables the detection of total amount of fluoride i.e. complex and uncomplex due to the interaction of TISAB (Itota *et al.*, 2004). Therefore, in studies where free and a low level of fluoride detection is the main objective, IC is preferred over ISE. Besides IC and ISE, capillary electrophoresis can be employed. It is more sensitive than IC but requires less volume of solution and offers higher separation efficiency (Yap *et al.*, 2002).

2.5: Fluoride recharge of restorative materials

The recharging capability of glass ionomer cements was first identified by Walls (Walls, 1986). Since then several studies have shown the recharge potential of glass ionomer based materials i.e. the capability to absorb fluoride from its surrounding and

re-release it. As discussed earlier, glass ionomer protects the tooth mainly due to its fluoride releasing property. In order to have a long term protection against cariogenic challenge these materials should possess a constant fluoride release mechanism. The fluoride release from glass ionomer based materials tends to taper off after a certain time period. Since the optimum amount of fluoride required for its protective action is yet to be determined (Creanor *et al.*, 1995), the need for constant recharge becomes mandatory to resist cariogenic challenges. It has also been suggested that material selection for high risk patients should be based on the fluoride release/uptake and not on the class of material (Preston *et al.*, 2003). During orthodontic treatment, white spot lesions are commonly encountered around brackets. Glass ionomer based materials are widely used as a bonding cement to prevent early caries attack in such patients due to their fluoride release and uptake property (Lin *et al.*, 2008).

The oral cavity is regularly exposed to fluoride in the form of mouth washes, dentifrices, and drinking water. In addition, the clinical sources of fluoride include the fluoridated gels and varnishes. These dentifrices and clinical fluoride applications contain high amount of fluoride which can act as the recharge sources for the GIC based materials. Studies have been conducted to prove and enhance the recharge capability of these materials; using either commercially available products or laboratory prepared solutions containing the amount of fluoride present in commercial products (Attar and Onen, 2002; Gao and Smales, 2001; Preston *et al.*, 1999; Rothwell *et al.*, 1998). Some studies conducted in the last 20 years are summarized in the following **Table 1.1**.

Table 1.1: *In vitro* studies done on the recharge of dental restoratives

Authors	Materials used	Initial release (Days)	Recharge medium	Recharge time (mins)	Re-release
Lin <i>et al.</i> ,2008	Vitremer (3M,USA) Fuji Ortho LC (GC, Japan) Ketac-Cem (3M, USA) Concise (3M, USA)	57	1.23%APF gel	4	14 days Re-exposure after 7 days
Hsu <i>et al.</i> ,2004	Fuji IX (GC, Japan) Vitremer (3M, USA) Z100 (3M, USA)	6	0.2% of NaF	1	1,1.5, 2, 3, 4, 6, 9, and 12 h
Itota <i>et al.</i> ,2004	Reactmer paste (Shofu, Japan) Dyract AP (Dentsply DeTrey, Germany) Xeno CF (Dentply-Sankin Co, Japan)	38	250ppm	60	8,16,23,30 th day Re-release measure for 2 days
Preston <i>et al.</i> ,2003	Chemfil (Dentsply, UK) Ketac Fil (ESPE, Germany) Vitrmer (3M,USA) PhotoFil aplicap (ESPE, Germany) Dyract (Dentsply, UK) Compoglass (Vivadent, Liechtenstein) Heliomolar (Vivadent, Liechtenstein) Concise (3M,USA)	8	500ppm NaF	2	720 days
Attar <i>et al.</i> ,2002	Ceramfil-b (PSP Bevelde, UK) Compoglass (Vivadent, Liechtenstein) Dyract (Dentsply, Germany)	60	1000 ppm NaF	-	Daily for 5 days

	Tetric (Vivadent, Liechtenstein) Valux plus (3M ,France)				
Coonar <i>et al.</i> , 2001	Concise (3M,USA) Fuji-Ortho-LC (GC, Japan) Limerick Glass (Limerick University)	42	2% of NaF	-	24,48 hours for 3 weeks
Gao <i>et al.</i> ,2001	GI-1 (hand mixed) (Shanghai Qingpu Dental Material Co, China) Ketac-Molar (ESPE, Germany) FX (Shofu, Japan) Hi-Dense (Shofu, Japan) Photac-Fi Photac-Fil Quick (ESPE, Germany) Hytac Aplitip (ESPE, Germany) Compoglass F (Vivadent, Liechtenstein) Z100 (3M,USA)	42	1.23% APF gel	4	42 days
De Witte <i>et al.</i> ,2000	ChemFil Superior (Dentsply, Germany) Fuji Cap II (GC, Japan) Ketac-Fil (ESPE, Germany) Hi Dense (Shofu, Japan) Fuji II LC capsule (GC, Japan) Photac-Fil (ESPE, Germany) Vitremmer (3M,USA)	21	2% NaF	60	35 days
Gao <i>et al.</i> ,2000	Fuji II LC (GC ,Japan) Fuji IX GP (GC ,Japan)	42	Protect (1.23%NaF) Karigel- N(Neutral)	4	42 days (1,2 days then weekly)

	Ketac Molar (ESPE, Germany)		1.1% NaF 0.001% CaF ₂ Mouth rinse		
Damen <i>et al.</i> , 1999	Fuji lining LC (GC, Japan)	90	1% NaF	5	1,2,3,7 days
Preston <i>et al.</i> , 1999	Chemfil (Dentsply, U.K) Ketac Fil (Espe, Germany) Vitremmer (3M, USA) Dyract (Dentsply) Heliomolar (Vivadent, Liechtenstein)	57	500 ppm NaF		57,64,120 th day
Strother <i>et al.</i> , 1998	Ketac-Fil (ESPE-Premier USA) Photac-Fil (ESPE-Premier USA) Tetric (Ivoclar, USA)	30	5000ppm NaF	4	Daily for 2 weeks Alternate days till 30 th day
Rothwell <i>et al.</i> , 1996	Dyract (Dentsply, Germany) Fuji II LC (GC, Japan) Vitremmer (3M, USA) Fuji IX (GC, Japan)	28 56	0.32%NaF tooth paste (Colgate- total)	60	1, 2,7 days Weekly for 2,3,4th week
Diaz- Arnold <i>et al.</i> , 1995	Ketac-Fil (ESPE, Germany) Ketac-Silver (ESPE, Germany) Photac-Fil (ESPE, Germany) Fuji II LC (GC, Japan)	35	Karigel-N (1.1 % NaF) Karigel (1.1 % APF) Omni Med – Natural (SnF ₂)	6	Daily for week 1 Daily for week 3 Daily for week 5 Repeated 3 more weeks

The recharge ability of glass ionomer cements has been tested against many different variables and the materials had positively responded to various topical fluoride treatments. Comparing the recharge ability of various aesthetic dental materials, glass ionomer based materials have proven better recharging capability than composites, which was found to be almost negligible (Forsten, 1991; Preston *et al.*, 2003). When conventional glass ionomer cement was compared against RMGIC, the dual cure

cement showed more recharge characteristics (Gao and Smales, 2001; Strother *et al.*, 1998). In yet another study, resin based materials like compomer, giomer and fluoride containing composites were analyzed, giomer showed the highest initial and long term release (Itota *et al.*, 2004). It can be concluded from several different studies that the materials which exhibit higher initial release are more likely to have higher uptake and re-release potential (Gao and Smales, 2001; Itota *et al.*, 2004).

The re-release usually follows the same pattern as of the initial release i.e. initial outburst followed by a slow release. The amount of fluoride released after recharge reaches pre-exposure levels within a few days (Attar and Onen, 2002). The exact mechanism of recharge is yet unknown and many theories have been put forward. De Witte *et al* (2000) postulated two different mechanisms of recharge. The first involves the simple diffusion of ions through the cement matrix which accounts for the short term release. During re-fluoridation, some amount of fluoride reacts with the intrinsic ions in the matrix, which are then released due to decomplexation and contributes to its long term release (De Witte *et al.*, 2000). Diaz-Arnold and co-workers suggest that it is a surface phenomenon, where the fluoride released after recharging was due to surface adsorption which later gets washed off (Diaz-Arnold *et al.*, 1995). Although several studies have indicated the re-charge potential and high release of fluoride in GIC based materials, yet it is still not known if the high release is solely due to the uptake from external sources. Hadley *et al* (1999) elucidated the mechanism by studying the uptake and re-release phenomenon separately and concluded that the re-release of ions after recharging was not more than what was

taken up thus nullifying the additional intrinsic release of fluoride (Hadley *et al.*, 1999).

2.6: Intraoral environment and physical properties of glass ionomer based materials

The intraoral environment is subjected to various chemical changes throughout the day. In normal physiological conditions, many factors contribute to the chemical variability, which could be extrinsic and intrinsic. Furthermore, inter and intra individual variations in the chemical environment are also evident. Dietary habits and frequency of food intake also plays an important role in influencing the chemical environment of the oral cavity. The carbohydrates from the dietary sources alter the chemical and biological balance and induce the cariogenic cycle. The acids produced by the plaque, acidic beverages, food and preventive agents are also crucial in altering the chemical balance of the oral cavity. Besides dietary habits, pathologies like bulimia, gastroesophageal reflux and anorexia produce acids of considerably low pH which causes dental erosion (Meurman and ten Cate, 1996).

In the oral cavity, the overlying plaque is representative of the undergoing chemical changes of saliva. As aforementioned, biofilms or plaque can be formed on any hard surfaces of the oral cavity and thus restorations are also of no exception. The pH /chemical changes in the overlying plaque increase the caries susceptibility of the enamel or dentine. Similarly, it also affects the surface properties of the underlying restorations (Fucio *et al.*, 2008). In general, all the materials are susceptible to degradation owing to the variations in oral cavity (Mohamed-Tahir and Yap, 2004)

and the individual responses to withstand the changes are found to be material dependent (Bollen *et al.*, 1997). The acidic challenges in the oral cavity have clinical implications, as rougher surfaces affect the aesthetics of restorative materials and encourage plaque accumulation (Bagheri *et al.*, 2007; Beyth *et al.*, 2008). The threshold surface roughness for bacterial retention has been mentioned as 0.2 μ m and below this, no further reduction in bacterial accumulation takes place (Bollen *et al.*, 1997).

The longevity of dental restoratives depends on the durability of materials and their properties (Jaeggi *et al.*, 2006). Numerous studies have been conducted to simulate the diverse environment of the oral cavity and to evaluate the resistance of materials to chemical degradation (Fukazawa *et al.*, 1987; Walls *et al.*, 1988; Yap *et al.*, 2000a) as well as biodegradation (Silva *et al.*, 2007). The resistance to dissolution of the materials have been measured by many parameters including surface roughness, wear and solubility tests. Among all the materials evaluated, the salt-based nature of glass ionomer makes it more prone to degradation than other restorative materials. It was postulated that the dissolution of glass ionomer could possibly be due to the acidic pH of the plaque, acidic food and beverages (Pluim and Arends, 1987). This was further explained as part of the buffering mechanism where the matrix forming ions are released in low pH (Czarnecka *et al.*, 2002). When compared under various food simulating liquids, GIC cements showed completed dissolution over the period of 3-6 months whilst RMGICs showed resistance to dissolution although its strength was reduced significantly (McKenzie *et al.*, 2003). The resin matrix of the dental composites tend to soften when exposed to organic acids and different dietary constituents (Wu *et al.*, 1984). It was also found that the dissolution of glass ionomer

based materials is not merely pH dependent but also rely on the chemical composition of the surrounding medium (McKenzie *et al.*, 2003).

The acidic environment has a pronounced effect on the fluoride release of glass ionomer based materials and fluoride release increases with decreasing pH. In high caries risk patients where the pH can be generally low, a material with high fluoride release is required to prevent caries and/or secondary caries. However, physico-mechanical properties can be compromised. While the latter is not an issue in Class V and some Class III cavities, use of these materials may be a concern in stress-bearing areas. Further clinical trials are required to study the long term durability and effect of glass ionomer based materials and to advocate their use in high risk patients.

Chapter 3: Scope of research

The overall aims of this research were as follows

- 1. To study the effect of maturation time on fluoride release and surface roughness**

In this phase, the fluoride release profiles of materials tested was determined with respect to maturation times of 10 mins, 30 mins and 24 hours. The effect of maturation time on the fluoride release and surface roughness was analyzed.

- 2. To study the effect of environmental pH on fluoride release profile and surface roughness**

The effect of intraoral environmental pH variability on the fluoride release profiles of the materials was determined. The effect of pH on surface roughness was also assessed.

- 3. To study the fluoride re-release profile of glass ionomer containing restoratives**

In phase 3, the fluoride uptake potential and re-release profile of glass ionomer containing restoratives were studied.

Chapter 4: Effect of maturation time on fluoride release and surface roughness

4.1: Introduction

Glass ionomer restoratives are acid base cements that set by the reaction of polyacrylic acids with ion leachable glass in an aqueous medium. The final product is a cross linked hydrogel matrix with glass filler particles (Crowley *et al.*, 2007; Nicholson, 1998). The protons from the acids react with the outer surface of glass particles and results in the leaching of metallic and non metallic ions. The carboxyl ions of the polyacrylic acids then react with the bivalent and trivalent ions forming calcium/polyacrylate salts followed by aluminium/polyacrylates salts, which are more stable and give final strength to the material. Traditional glass particles contain calcium as the main component. Newer GIC contains strontium based glass. As the ionic radii of calcium and strontium are similar, no difference was found between strontium-carboxylate and calcium-carboxylate polysalts (Deb *et al.*, 1999). During the initial setting, the material is not only sensitive to hydration but also to dehydration. In the oral cavity, early exposure of the mixed cement to moisture is unavoidable and has shown to adversely affect the mechanical properties of the materials (Causton, 1981). To protect conventional glass ionomers from early moisture exposure, a layer of unfilled resin is applied onto the surface of restorations. However, no significant difference in strength was found between resin coated and uncoated samples with early exposure to moisture (Wang *et al.*, 2006). Another study showed that the shear punch strength was actually improved with uncoated samples (Leirskar *et al.*, 2003). To overcome the early moisture sensitivity of glass ionomer

cements, a modification was incorporated using resin. The moisture sensitivity problem was avoided as the initial setting was achieved by light cure polymerization in RMGIC.

Fluoride is among the non-networking ions of the set cement. During the setting phase, the ions become a part of the set matrix and slowly diffuses out from the surface (Verbeeck *et al.*, 1998). The diffusion of fluoride from GICs has given the material its unique cariostatic and antibacterial properties. Interference in the cement maturation due to moisture contamination can result in a higher amount of fluoride release, producing set cement with inferior mechanical properties (Crisp *et al.*, 1980a). Coating the restorations with unfilled resin for moisture protection can invariably reduce the amount of fluoride release (Hattab and Amin, 2001), which is not desirable in high risk patients. Although RMGICs are supposedly less moisture sensitive, early exposure to moisture has shown to affect the short and long term fluoride release (Marks *et al.*, 2000). Giomer, a hybrid of glass ionomer and resin composite, is a relatively new type of tooth coloured restorative material. The material has shown good aesthetics, handling characteristics and fluoride release. No studies have been conducted to analyze the effect of maturation time on the fluoride release and its effect on the surface properties of Giomer.

The objectives of this study were to determine the following

- Fluoride release profile of glass ionomer containing cements
- Effect of maturation time on fluoride release
- Effect of early moisture exposure on the surface roughness.

4.2: Materials and Methods

The materials used in this study are listed in **Table 4.1**. The choice of materials includes highly viscous glass ionomer, resin modified glass ionomer and Giomer. Two HVGICs (Fuji IX-Extra [FE] and Fuji IX-Fast [FF], GC Japan) are selected as both belong to the same group but have a different chemistry which makes one material set faster and the other to release higher amounts of fluoride. RMGIC (Fuji II LC [FL], GC Japan) and Giomer (Beautifil II [BF], Shofu Japan) were also selected to compare and observe the fluoride release profile as a function of maturation time. Except for BF, the rest of the materials are encapsulated. All materials were mixed according to manufacturers' instructions. The mixed materials were injected into the cylindrical recess of stainless steel moulds (8.5mm diameter, 1 mm thick) and covered with cellulose strips. The filled moulds were then kept between two glass slides and hand pressure was applied to extrude excess material and to obtain a smooth surface finish. After initial setting, the excess material was removed using a scalpel. Light cured materials were polymerized using Curing light Light 2500 (3M ESPE, Germany). The samples (n=6) of each material were allowed to set at $\pm 37^{\circ}\text{C}$ in 99% humidity simulating the oral environment for 10 mins, 30 mins and 24 hours. According to manufacturer's instruction, the initial setting time of the HVGIC was between 2-3 mins at 37°C . This was difficult to achieve in laboratory room temperature which was usually maintained at $23\text{-}24^{\circ}\text{C}$. At this temperature the initial setting was achieved in 10 mins, hence it was taken as the initial setting time of the material. The complete setting of the material was represented by 24 hours matured samples.

The individual specimens were suspended with the help of a dental floss in 15ml of immersion medium (deionized water) in polystyrene containers and transferred to a shaking incubator with a temperature of 37°C at the speed of 40 rpm. The immersion medium was changed weekly for 4 weeks. Every week, the specimens were removed from the medium, blotted in tissue paper and surface roughness Ra was determined using a profilometer (Surftest, Mitutoyo Corp, Tokyo, Japan) with a probe diameter of 5µm. The probe couldn't record the changes under 5µm and this was the limitation of the study. Three readings at different areas were taken for each specimen and the mean was tabulated.

Table 4.1: Profiles of materials investigated

Materials	Batch Number	Shade	Manufacturer	Type	Curing method	Clinical Application
Fuji IX Extra (FE)	805141	A2	GC Asia, Japan	HVGIC	Chemical	Restorative
Fuji IX Fast (FF)	8052901	A2	GC Asia, Japan	HVGIC	Chemical	Restorative
Fuji II LC (FL)	907087	A2	GC Asia, Japan	RMGIC	Light	Restorative
Beautiful II (BF)	60984	A2	Shofu, Japan	Giomer	Light	Restorative

The weekly analysis of fluoride from the collected samples was carried out using the Combination Ion Selective Electrode (Model 9609 BNWP, Orion Research, Beverly, USA). For the fluoride ion measurement, the standards were prepared using 100 ppm of NaF standard (Orion Research, Beverly, USA). Three point calibration of the meter was carried out using 0.1, 1 and 10 ppm (part per million) of standards prepared from 100 ppm of NaF mixed with equal volumes of TISAB II (Orion Research, Beverly,

USA). The slope achieved between -54mV to -60mV was used to carry out the analysis. To analyze fluoride ions released, equal volumes of sample and TISAB II (5ml) were mixed together and the readings were recorded in ppm (parts per million). The meter was calibrated before taking the readings and re-checked after every 10 readings to ensure the accuracy of the meter. Data were analyzed using Univariate General Linear Model (GLM) with Post Hoc Tukey's test. Further one way ANOVA and Post Hoc Scheffe's was performed at significance level of 0.05 to analyze the difference among each group of material with respect to maturation time and evaluation period. Pearson's correlation analysis between fluoride release and surface roughness was also performed at significance level 0.05.

4.3: Results

Mean fluoride release (ppm) and surface roughness Ra (μm) of the materials for 10, 30 mins and 24 hours maturation times are shown in **Tables 4.2** and **4.3**. The results of the statistical analysis are reflected in **Tables 4.4 – 4.6**.

Univariate GLM showed significant differences among materials ($p < 0.05$), maturation times ($p < 0.05$) and evaluation periods ($p < 0.05$). For all the evaluation period and maturation time FE showed the highest fluoride release followed by FF, FL and BF. Among the maturation times, 10 mins showed significantly higher release followed by 30mins and 24 hours. The highest release of fluoride was observed in the first week whereas week 3 and 4 showed no significant difference for all the materials evaluated.

FE and FF were generally rougher than FL and BF at all time periods. For all materials, specimens matured for 24 hours were generally rougher than those matured for 10 and 30 mins. No marked difference in Ra values were observed between the latter.

For the maturation time of 10 mins, FE released the highest amount of fluoride and BF released the lowest amount of fluoride. No statistically significant difference was observed among FF, FL and BF. The trend was similar for 30 mins maturation time. However, during weeks 3 and 4, a significant difference was observed between materials and fluoride release was found to be highest for FE followed by FF, FL and BF. When tested for materials and evaluation times, 10 mins maturation time resulted in the highest release of fluoride and it was the least for 24 hrs. However, no statistically significant difference was observed for BF.

For FE, 10 mins maturation time generally resulted in rougher specimens. For FL it was 24 hours maturation. Significant differences in surface roughness between materials varied with maturation and evaluation time. For 10 mins maturation time, FE was generally significantly rougher than FL, BF. FE also had significantly higher Ra values than BF when allowed to mature for 30 mins before moisture exposure. At weeks 2, 3 and 4, FF was significantly rougher than BF for 24 hours maturation time. The correlation between fluoride release and surface roughness was low ($r=0.083$) and insignificant.

Table 4.2: Mean amount of fluoride release after maturation times of 10 mins, 30 mins and 24 hours (standard deviations are given in parenthesis).

Materials	Maturation time	Fluoride Release (ppm)			
		7 Days	14 Days	21 Days	28 Days
FE	10 mins	54.90 (13.37)	16.87 (5.40)	10.40 (3.34)	7.06 (2.00)
	30 mins	15.87 (1.37)	5.15 (0.50)	2.50 (0.22)	1.80 (0.15)
	24 hrs	12.83 (1.67)	3.54 (0.62)	2.30 (0.43)	1.72 (0.27)
FF	10 mins	10.21 (2.50)	2.74 (0.72)	1.52 (0.51)	1.15 (0.40)
	30 mins	7.15 (0.41)	2.56 (0.24)	1.43 (0.17)	1.03 (0.16)
	24 hrs	4.46 (0.28)	1.24 (0.06)	0.88 (0.03)	0.70 (0.02)
FL	10 mins	9.20 (1.13)	3.26 (0.26)	2.51 (0.12)	1.74 (0.12)
	30 mins	6.17 (0.88)	2.51 (0.34)	2.00 (0.30)	1.51 (0.25)
	24 hrs	4.12 (0.57)	1.40 (0.25)	1.00 (0.10)	0.78 (0.07)
BF	10 mins	0.42 (0.06)	0.12 (0.03)	0.10 (0.02)	0.05 (0.01)
	30 mins	0.38 (0.07)	0.14 (0.03)	0.06 (0.01)	0.07 (0.01)
	24 hrs	0.51 (0.11)	0.10 (0.01)	0.06 (0.01)	0.05 (0.01)

Table 4.3: Mean values of Ra after maturation times of 10 mins, 30 mins and 24 hours (standard deviations are given in parenthesis).

Materials	Maturation time	Surface Roughness Ra (μm)				
		Before	Week 1	Week 2	Week 3	Week 4
FE	10 mins	0.03 (0.01)	0.07 (0.01)	0.08 (0.01)	0.06 (0.02)	0.10 (0.01)
	30 mins	0.03 (0.004)	0.04 (0.01)	0.07 (0.01)	0.07 (0.01)	0.08 (0.01)
	24 hrs	0.03 (0.01)	0.04 (0.01)	0.05 (0.004)	0.06 (0.01)	0.07 (0.01)
FF	10 mins	0.03 (0.005)	0.06 (0.01)	0.06 (0.01)	0.06 (0.01)	0.10 (0.01)
	30 mins	0.03 (0.003)	0.05 (0.01)	0.06 (0.01)	0.06 (0.01)	0.07 (0.02)
	24 hrs	0.02 (0.004)	0.06 (0.01)	0.10 (0.01)	0.10 (0.01)	0.10 (0.01)
FL	10 mins	0.02 (0.004)	0.03 (0.01)	0.04 (0.01)	0.04 (0.01)	0.06 (0.01)
	30 mins	0.02 (0.005)	0.06 (0.005)	0.05 (0.01)	0.05 (0.01)	0.05 (0.01)
	24 hrs	0.02 (0.004)	0.05 (0.01)	0.06 (0.01)	0.07 (0.004)	0.07 (0.01)
BF	10 mins	0.01 (0.004)	0.03 (0.01)	0.03 (0.005)	0.03 (0.01)	0.04 (0.01)
	30 mins	0.02 (0.004)	0.02 (0.005)	0.04 (0.01)	0.04 (0.01)	0.05 (0.01)
	24 hrs	0.02 (0.004)	0.03 (0.01)	0.04 (0.01)	0.04 (0.01)	0.05 (0.01)

Table 4.4: Comparison of fluoride release between different maturation times (>indicates statistically significant difference and NS indicates no significant difference)

Days	FE	FF	FL	BF
7	10 >30, 24	10 > 30 >24	10 >30 >24	NS
14	10 >30, 24	10, 30 >24	10 >30 >24	10, 30 > 24
21	10 >30, 24	10, 30 >24	10 >30 >24	10, 30 >24
28	10 >30, 24	10 >30, 24	10 >30 >24	NS

Table 4.5: Comparison of fluoride release between different materials (>indicates statistically significant difference and NS indicates no significant difference)

Days	10mins	30mins	24hours
7	FE > FF , FL , BF	FE > FF , FL > BF	FE > FF , FL > BF
14	FE > FF , FL , BF	FE , FL, FF > BF	FE , FF , FL > BF
21	FE > FF , FL , BF	FE > FL > FL > BF	FE > FF , FL > BF
28	FE > FF , FL , BF	FE > FF > FL > BF	FE > FF , FL > BF

Table 4.6: Comparison of surface roughness between different materials (>indicates statistically significant difference and NS indicates no significant difference)

Days	10mins	30mins	24hours
7	FE, FF > FL > BF	FE, FF > FL, BF	FE > FF, FL > BF
14	FE, FF > FL, BF	FE, FF, FL > BF	FF > FE, FL, BF
21	FE, FF > BF	FE > FL, BF	FF > FE, FL, BF
28	FF, FE > FL, BF	FE > FL > BF	FF > FE , BF

Table 4.7: Comparison of surface roughness between different maturation times (>indicates statistically significant difference and NS indicates no significant difference)

Days	FE	FF	FL	BF
7	10 > 30, 24	10, 30 > 24	24 > 10, 30	NS
14	10, 30 > 24	30 > 24	24 > 10	NS
21	NS	24 > 10, 30	NS	NS
28	10 > 24	NS	24 > 30	NS

Fig 4.1: Mean amount of fluoride release from FE, FF, FL and BF after 10 mins of maturation time.

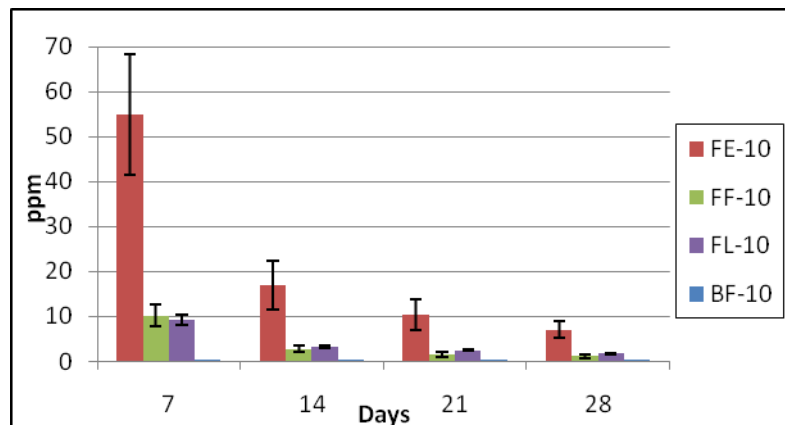


Fig 4.2: Mean amount of fluoride release from FE, FF, FL and BF after 30 mins of maturation time.

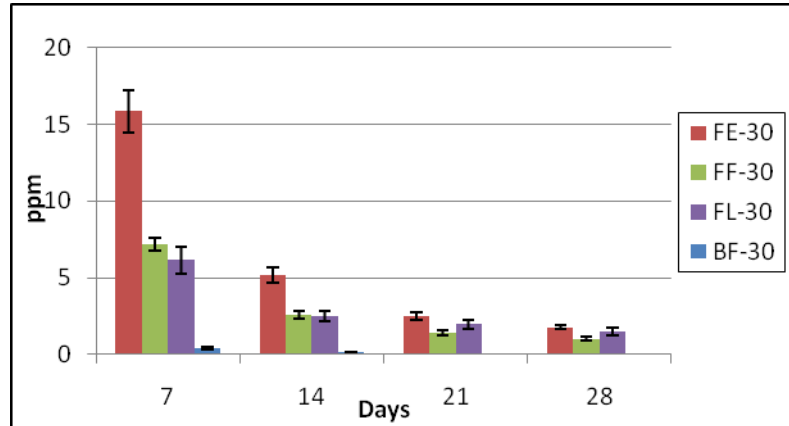
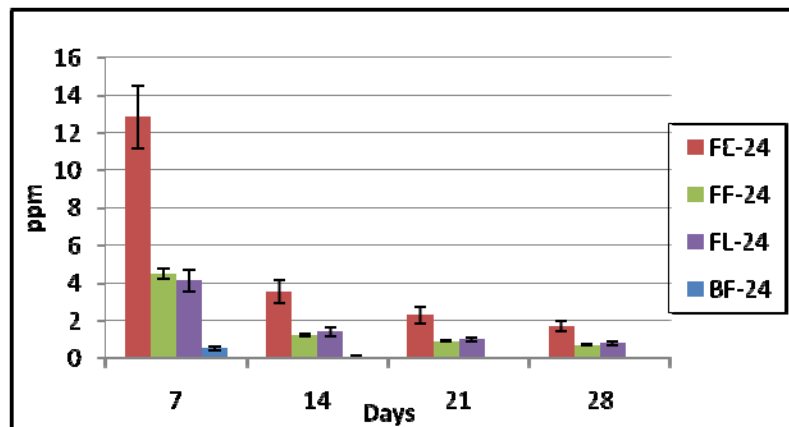


Fig 4.3: Mean amount of fluoride release from FE, FF, FL and BF after 24 hours of maturation time.



4.4: Discussion

Fluoride has shown to remineralise decayed tooth structure after caries attack, prevent demineralization by strengthening tooth structure and possess antibacterial properties. To prevent secondary caries, many restorative materials are developed with fluoride as part of their chemistry. Silicate cements were the first to show fluoride release. Due to their inadequate mechanical properties, they were soon replaced by glass ionomer cements. Glass ionomer cements have gained popularity due to their unique properties including chemical adhesion, biocompatibility and fluoride release. The glass component essentially contains fluoride and is responsible for the long term fluoride release.

Immersion mediums utilized to study the release of fluoride include deionized water, artificial saliva and human saliva (Wiegand *et al.*, 2007). The release pattern was found to be similar in most studies. The quantity, however, varied ranging from the highest release in deionized water to lowest release in human saliva (Hayacibara *et al.*, 2004). Strictly adhering with the objectives of the study and technicalities involved in human saliva, deionized water was selected as the immersion medium in this study. Less maturation time and early exposure to moisture is also expected to produce material with inferior mechanical properties.

The glass ionomer containing restoratives evaluated are widely used in Class V cavities for root caries, atraumatic restorations, sandwich techniques and in the primary dentition. Glass ionomers are prone to early moisture sensitivity resulting in lowered mechanical properties and increased fluoride release due to dissolution. Being hydrophilic and acid base in nature, they are prone to degradation if

contaminated during the initial setting phase. Clinically, early moisture control is difficult to control and coating a material with resin can reduce the amount of fluoride release, which is not desirable in high risk patients. In this study, uncoated specimens and deionized water as an immersion medium were used as it extracts more fluoride. Three different maturation times were selected i.e. 10 mins, 30 mins and 24 hours. For chemically cured materials, the recommended setting time was in the range of 2-3mins at 37⁰C. A 10 mins maturation time was needed for initial setting in the laboratory, due to the lower room temperature of 23-25⁰C.

The maximum amount of fluoride released from all the materials was observed during the first week. Previous studies have shown initial fluoride release to be the highest during the first few days followed by a gradual slow-down (Carvalho and Cury, 1999; Diaz-Arnold *et al.*, 1995). The high amount of fluoride released during the first week supports earlier studies and the “initial burst” phenomenon. Fluoride release from highest to lowest was in this order FE> FF> FL >BF for all the evaluated times. As extrinsic factors (temperature and immersion medium) remained constant throughout the study period, it is the intrinsic chemistry and content of fluoride that dictated the amount of fluoride released. Kuhn and Wilson (1985) postulated dissolution to be a surface wash off phenomenon followed by diffusion from pores and crack and bulk diffusion. Previous studies have indicated a trend for fluoride release among the glass ionomer containing restoratives, conventional GICs being capable of releasing the highest amount of fluoride (Carvalho and Cury, 1999; Yap *et al.*, 2002). The results of our study corroborated these studies as the two HVGICs released the highest amount of fluoride for all the maturation times. The adjective ‘Extra’ had been given to FE by the manufacturer as it was designed to release higher amounts of fluoride and the

amount released was more than FF (which belongs to the same category and manufactured by the same company). Information was not available regarding the intrinsic amount of fluoride of the two materials. However, according to the manufacturer, FE contains specially formulated fluoroaluminosilicate glass which has a higher amount of fluoride compared to FF. As a result, the gel layer outside the glass particles releases an extra amount of fluoride.

Although some studies have shown equal potential of RMGICs and GICs to release fluoride (Forsten, 1998; Mitra, 1991; Momoi and McCabe, 1993), this was not observed in our research. Both HVGICs released more fluoride than RMGICs which was in agreement with the work of Diaz-Arnold (1995). The difference is possibly because of the simultaneous polymerization reaction in RMGICs that enables the initial setting of the material and inhibits the dissolution of the cement. Another possible reason is the lower content of fluoride in RMGICs to control translucency (Wilson, 1990). Loosely bound fluoride from the cement's pore liquid was held responsible for the short term release whilst the long term was considered to be due to diffusion of the strongly bound fluoride from the matrix (Marks *et al.*, 2000). Giomer released the least fluoride amongst the glass ionomer containing materials. This could be due to the use of pre-reacted particles embedded in resin matrix. The release of fluoride due to early water exposure is influenced by the setting chemistry (Marks *et al.*, 2000). Materials which set by acid base reaction released more fluoride and decreases as the polymerization reaction predominates over the setting chemistry.

The maturation time greatly influenced the fluoride releasing profiles of the material investigated. For all the materials, 10 mins of maturation time generally released more amount of fluoride than 30 mins and 24 hours. During the acid base reaction, H⁺ ions

from the acid cause the liberation of many network and non network forming ions from the glass particles. Any exposure to moisture can lead to dissolution of the materials by leaching of different ions including fluoride. It is thought that early moisture contact causes polyacrylic acids and glass particles to bind with water molecules and hinders initial setting (Mojon *et al.*, 1996). For FE, no difference was observed between 30 mins and 24 hours matured specimens, as the critical time required for initial setting is 30 mins after which no effect was observed. Mojon *et al* (1996) advised that glass ionomers be protected from early moisture contact for at least 15 mins. Another study has shown that 15 mins matured samples of conventional GICs released more fluoride than 24 hours and 1 week matured samples (Verbeeck *et al.*, 1998). Although RMGICs showed less sensitivity towards moisture than conventional GICs, early moisture sensitivity cannot be neglected. Varnish or a resin coating has also been advised for RMGICs to reduce moisture sensitivity (Williams *et al.*, 2001). In our study, the maturation time of 10 mins showed the highest release from FF followed by 30 mins and 24 hours. Acid base reaction initiates the dual cure setting mechanism of RMGICs and is later masked by the polymerization reaction. The effect of maturation time for RMGICs is in accordance with the results of Verbeeck *et al* (1998), where immediately cured samples showed more release of fluoride than samples matured for 24 hours. Thus exposure to water during early setting can affect the fluoride release.

For BF, maturation time had no effect on the fluoride release. Gionomers are similar to composite resin except for the addition of pre-reacted glass ionomer particles. The release of fluoride is more diffusion controlled from the matrix and dependent on water sorption and segmental mobility of polymer chains (Ikemura *et al.*, 2008).

No difference in surface roughness was observed for the two HVGICs i.e. FE and FF. FE contain extra fluoride as part of its chemistry whereas FF is designed to have a fast set. Fluoride is a non-networking ion of glass ionomer cement and its release does not affect the physico-mechanical properties. In this study, no correlation was found between fluoride release and surface roughness. This could be due to the fact that besides fluoride, many other networking ions could be leached due to early moisture contamination and possibly leading to decreased mechanical properties (Oilo, 1992). The two HVGICs showed increased Ra for the maturation time of 10 mins than the rest of the materials which indicates the moisture sensitivity of acid-base cements. Except for week 1, no difference was observed in FL and BF. Both materials contain resin and polymerization reaction as part of their setting chemistry. Similarly, no effect of maturation was observed. In giomers, the pre-reacted glass phase releases fluoride through ligand exchanges and does not affect the matrix-resin interface (Tay *et al.*, 2001). The increase of surface roughness from giomers to glass ionomer cements is indicative of the nature of the cements as acid base cements possess more hydrophilicity than resin based materials.

4.5: Conclusions

Among the fluoride containing glass ionomer cements, HVGICs released the most amount of fluoride during the different time periods, followed by RMGIC and Giomer. HVGICs should be protected with a resin coating coating for at least 30 mins prior to moisture exposure. As the setting chemistry of the materials shifts from acid-base to resin polymerization, less fluoride release and lower surface roughness was observed. As the amount of fluoride reduces with time, the long term fluoride recharge potential of these materials should be investigated.

Chapter 5: Effect of environmental pH on fluoride release profile and surface roughness

5.1: Introduction

The resistance of the materials to different physical, chemical and biological degradation is dependent on their chemistry and surface properties. The oral cavity is subjected to various extrinsic and intrinsic acidic challenges. The clinical success and longevity of these materials depend on the material's ability to withstand erosive attacks that can decrease physico-mechanical properties.

Vomiting and regurgitation can lead to the passage of gastric acids back into the oral cavity. Pathologies associated with aforementioned include oesophageal reflux, bulimia, anorexia nervosa and alcohol abuse (Munoz *et al.*, 2003). The passage of intrinsic acids of which the pH could be lower than 1 can cause detrimental effects on the teeth as well as restorative materials (Oh *et al.*, 2002). Extrinsic acids, environmental (Wiegand and Attin, 2007) and/or dietary, can potentially cause erosive attacks on the surfaces of restorative materials as the pH could range from 2.48 to 3.20 (Wan Bakar and McIntyre, 2008).

All the hard surfaces in the mouth, natural or artificial i.e. dental materials, are susceptible to biofilm/plaque formation. The intake of fermentable carbohydrates can bring down the pH of the overlying plaque to 4 consequently inducing a cariogenic cycle (Muhlemann *et al.*, 1977). The frequent provision of fermentable carbohydrates can therefore also decrease the pH of the overlying biofilm for long periods of time, which in turn damages the surface of underlying restorative materials (Fucio *et al.*,

2008). Thus the integrity of the surfaces of the restorative materials could be compromised due to biological and chemical degradation.

Besides affecting the physical properties, fluoride release was has found to increase with the decreasing pH and was postulated to be pH controlled (Carvalho and Cury, 1999). The hydrolytic degradation of matrix can take place at neutral pH whereas acidic pH can in turn remove the gelatinous layer of matrix and the filler particles (Fano *et al.*, 2001). Various studies have been conducted to explore the kinetics of fluoride release in an acidic medium. Not only fluoride but the release of other networking ions considerably increased in acidic pH (Czarnecka *et al.*, 2002). Low pH makes glass ionomer cements release more fluoride that is clinically important to minimize secondary caries (Carey *et al.*, 2003). Although the high amounts of fluoride release has been associated with cariostatic and antimicrobial action (De Moor *et al.*, 2005; Hayacibara *et al.*, 2004), acidic environments also have detrimental effect on the surface of materials (Turssi *et al.*, 2002). Rough surfaces have high surface energy and are more susceptible for bacterial attachment, exacerbating plaque accumulation (Hannig, 1999) that not only can cause secondary caries but also induce periodontal inflammation. The aesthetics of the materials is also largely affected by the roughness of the surface.

The effect of food stimulating liquids and pH on restorative materials has been widely studied (Turssi *et al.*, 2002; Yap *et al.*, 2000a). Changes in surface characteristics had been reported and response was marked with decreased pH (Turssi *et al.*, 2002). A material with long term fluoride release and ability to withstand a harsh chemical environment would be an ideal restorative material especially in xerostomic and high caries risk patients.

Clinically, many factors which are extremely difficult to replicate in *in vitro* can contribute to the degradation of the material. *In vitro* studies are usually conducted to isolate specific *in vitro* factors and assess the durability of the restorative materials. In this study, the chemical degradation of materials with a wide range of pH simulating different clinical conditions of the oral cavity was undertaken. The immersion medium was a demineralising solution representing artificial saliva of pH 2.5, 3.5 and 4.5 using modified 1M HCL. In the earlier studies, composite resins have shown the highest resistance to acidic degradation and conventional glass ionomer has shown the least. The effects of pH on Giomers have not been widely studied. Accelerated testing involving exposure of materials for extended time periods *in vitro* and this has been employed in many previous studies (McKenzie *et al.*, 2003; Yap *et al.*, 2000a; Yap *et al.*, 2000b) as it is extremely difficult to extrapolate *in vivo* situation in an *in vitro* study.

The objectives of this study were to determine the

- Effect of environmental pH on fluoride release profile
- Effect of pH on surface roughness
- Effect of fluoride release on surface roughness

5.2: Materials and Methods

The fluoride containing restorative materials investigated included two HVGICs (Fuji IX Extra [FE], Fuji IX Fast [FF]) a RMGIC (Fuji II LC [FF]) and a Giomer (Beautiful II [BF]). The profiles of the materials are listed in **Table 5.1** and represent the more commonly used glass ionomer containing restoratives. Except for BF, the rest of the materials were encapsulated. All materials were mixed according to manufacturers'

instructions. The mixed materials were injected into the cylindrical recess stainless steel moulds (8.5mm diameter, 1 mm thickness) and covered with cellulose strips. The filled moulds were then kept between two glass slides and hand pressure was applied to extrude excess material and to obtain a smooth surface finish. After the initial setting, the excess material was removed using a scalpel. The light cured materials were polymerized using Curing Light 2500 (3M ESPE, Germany) for 40 secs. The samples were allowed to set at $\pm 37^{\circ}\text{C}$ in 99% humidity simulating oral environment for 24 hours. Six disc shaped specimens ($n=6$) of each material were randomly divided into three groups. To observe the effect of various acidic environments, the immersion medium employed was a demineralising solution prepared according to ten Cate's protocol (ten Cate and Duijsters, 1982). The pH of the demineralising solution was adjusted to 2.5, 3.5 and 4.5 by adding 1 M HCl solution (Appendix). The individual specimens were suspended with the help of a dental floss in 15 ml of immersion medium in polystyrene containers and transferred to the shaking incubator with a temperature of 37°C at the speed of 40 rpm.

The immersion mediums were changed weekly for 4 weeks. Every week the specimens were removed from the medium blotted in tissue paper and the surface roughness R_a (μm) was observed using a profilometer (Surftest, Mitutoyo Corp, Tokyo, Japan) with a probe diameter of $5\mu\text{m}$. Three readings at different spots were taken on each specimen and the mean R_a calculated. The specimens were then placed in polystyrene containers containing freshly prepared demineralising solution.

The weekly analysis of fluoride from the collected samples was carried out using the Combination Ion Selective Electrode Model 9609 BNWP (Orion Research, Beverly,

USA). For the fluoride ion measurement, the standards were prepared using 100 ppm of NaF standard (Orion Research, Beverly, USA). Three point calibration of the meter was carried out using 0.1, 1 and 10 ppm (part per million) of standards prepared from 100 ppm of NaF mixed with equal volume of Total ionic strength adjustment buffer TISAB II (Orion Research, Beverly, USA) . The slope achieved between -54mV to -60mV was used to carry out the analysis. To analyze the released fluoride ions, equal volumes (5ml) of the sample and TISAB II were mixed together and the readings were recorded in ppm (parts per million). Data were analyzed using Univariate General Linear Model (GLM) and Post Hoc Tukey's test as well as one way ANOVA and post hoc Scheffe's ($p < 0.05$).

Table 5.1: Profile of the materials investigated

Materials	Batch Number	Shade	Manufacturer	Type	Curing method	Clinical Application
Fuji IX Extra (FE)	805141	A2	GC Asia, Japan	HVGIC	Chemical	Restorative
Fuji IX Fast (FF)	8052901	A2	GC Asia, Japan	HVGIC	Chemical	Restorative
Fuji II LC (FL)	907087	A2	GC Asia, Japan	RMGIC	Light	Restorative
Beautifil II (BF)	60984	A2	Shofu, Japan	Giomer	Light	Restorative

5.3: Results

Table 5.2-4 shows the mean amount of fluoride released from materials at different pH. **Table 5.7-9** shows the mean Ra observed with the materials. Results of statistical analysis are reflected in **Table 5.6-7**.

Univariate GLM showed significant differences among materials ($p < 0.05$), pH ($p < 0.05$), evaluation periods ($p < 0.05$). For all the pH and evaluation times, FE showed the highest release of fluoride followed by FF, FL and BF. In pH 2.5 all materials showed increased Ra where as 4.5 showed the least the fourth week. Among the materials FE and FF showed higher surface roughness than FL and BF. The correlation between fluoride release and surface roughness was weak ($r = 0.45$) but significant at $p < 0.01$.

For all pH and evaluation times, fluoride released from FE was the highest followed by FF, FL and BF. The amount of fluoride released varied between materials and was noted to be highest in the first week. When the pH of mediums were compared, the amount of fluoride released was highest for pH 2.5 followed by 3.5 and 4.5.

Significant differences in the Ra values varied with pH and evaluation times. For pH 4.5, FE was generally significantly rougher than FL, BF. For pH 3.5, FE and FF had significantly higher Ra values than all the other materials at all evaluation times. For pH 2.5, FE was significantly rougher than all the other materials from week 2 onwards.

Table 5.2: Mean amount of fluoride release (ppm) at pH 4.5 (standard deviations are given in parenthesis).

Materials	7days	14days	21days	28days
FE	12.30 (0.60)	8.83 (0.54)	7.84 (0.31)	5.67 (0.20)
FF	6.20 (0.25)	2.37 (0.14)	1.64 (0.33)	1.10 (0.05)
FL	3.45 (0.56)	1.31 (0.20)	1.31 (0.20)	0.90 (0.06)
BF	1.52 (0.51)	0.51 (0.16)	0.31 (0.08)	0.32 (0.07)

Table 5.3: Mean amount of fluoride release (ppm) at pH 3.5 (standard deviations are given in parenthesis).

Materials	7days	14days	21days	28days
FE	16.70 (1.76)	12.40 (1.32)	5.12 (0.33)	4.50 (0.41)
FF	9.11 (0.71)	3.00 (0.40)	2.57 (0.23)	1.07 (0.07)
FL	9.16 (0.86)	3.60 (0.37)	2.80 (0.37)	2.47 (0.35)
BF	1.84 (0.20)	0.60 (0.06)	0.53 (0.06)	0.54 (0.03)

Table 5.4: Mean amount of fluoride release (ppm) at pH 2.5 (standard deviations are given in parenthesis).

Materials	7days	14days	21days	28days
FE	26.70 (1.61)	23.70 (2.14)	22.06 (3.21)	22.33 (3.33)
FF	12.50 (0.87)	11.17 (1.01)	10.28 (0.64)	8.75 (0.65)
FL	11.40 (1.10)	8.13 (0.75)	8.08 (1.15)	8.46 (0.42)
BF	4.85 (0.50)	1.60 (0.14)	1.56 (0.10)	1.54 (0.05)

Table 5.5: Comparison of fluoride release between different acidic pHs (> indicates statistically significant difference).

Days	FE	FF	FL	BF
7	2.5 > 3.5 > 4.5	2.5 > 3.5 > 4.5	2.5 > 3.5 > 4.5	2.5 > 3.5, 4.5
14	2.5 > 3.5 > 4.5	2.5 > 3.5 > 4.5	2.5 > 3.5 > 4.5	2.5 > 3.5, 4.5
21	2.5 > 4.5, 3.5	2.5 > 3.5 > 4.5	2.5 > 3.5 > 4.5	2.5 > 3.5 > 4.5
28	2.5 > 3.5, 4.5	2.5 > 3.5, 4.5	2.5 > 3.5 > 4.5	2.5 > 3.5 > 4.5

Table 5.6: Comparison of fluoride release between different materials (> indicates statistically significant difference).

Days	pH 4.5	pH 3.5	pH 2.5
7	FE> FF> FL> BF	FE> FF> FL> BF	FE> FF> FL> BF
14	FE> FF> FL, BF	FE> FF, FL> BF	FE> FF> FL> BF
21	FE > FF> FL> BF	FE> FF , FL> BF	FE > FF> FL> BF
28	FE> FF> FL> BF	FE> FF> FL> BF	FE> FF, FL> BF

Table 5.7: Mean Ra (μm) at pH 4.5 (standard deviations are given in parenthesis).

Materials	Before	Week 1	Week 2	Week 3	Week 4
FE	0.11 (0.08)	0.16 (0.11)	0.18 (0.05)	0.29 (0.14)	0.33 (0.07)
FF	0.06 (0.01)	0.14 (0.07)	0.12 (0.04)	0.16 (0.07)	0.18 (0.02)
FL	0.07 (0.04)	0.05 (0.02)	0.06 (0.02)	0.07 (0.02)	0.06 (0.01)
BF	0.06 (0.03)	0.04 (0.02)	0.07 (0.05)	0.06 (0.03)	0.06 (0.03)

Table 5.8: Mean Ra (μm) at pH 3.5 (standard deviations are given in parenthesis).

Materials	Before	Week 1	Week 2	Week 3	Week 4
FE	0.03 (0.01)	0.15 (0.004)	0.28 (0.04)	0.39 (0.02)	0.48 (0.02)
FF	0.03 (0.004)	0.21 (0.03)	0.27 (0.03)	0.34 (0.03)	0.41 (0.01)
FL	0.04 (0.005)	0.07 (0.03)	0.07 (0.01)	0.18 (0.06)	0.24 (0.02)
BF	0.03 (0.01)	0.06 (0.01)	0.09 (0.01)	0.11 (0.01)	0.14 (0.02)

Table 5.9: Mean Ra (μm) in pH 2.5 (standard deviations are given in parenthesis).

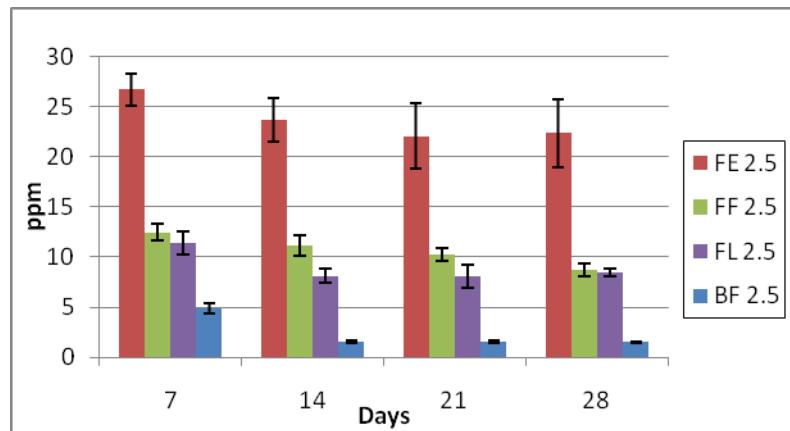
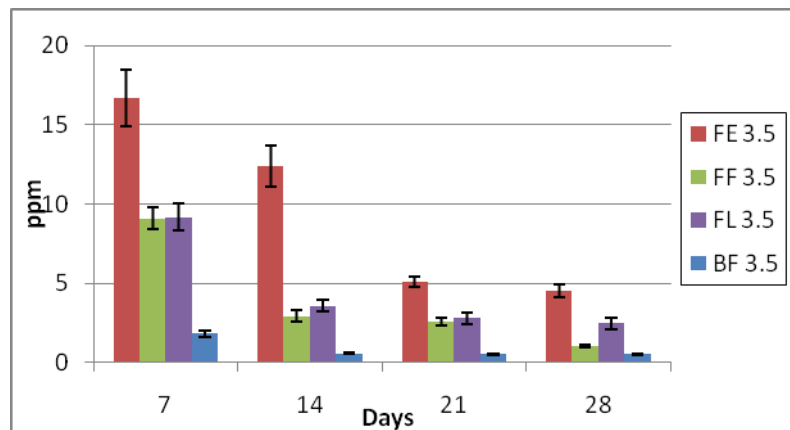
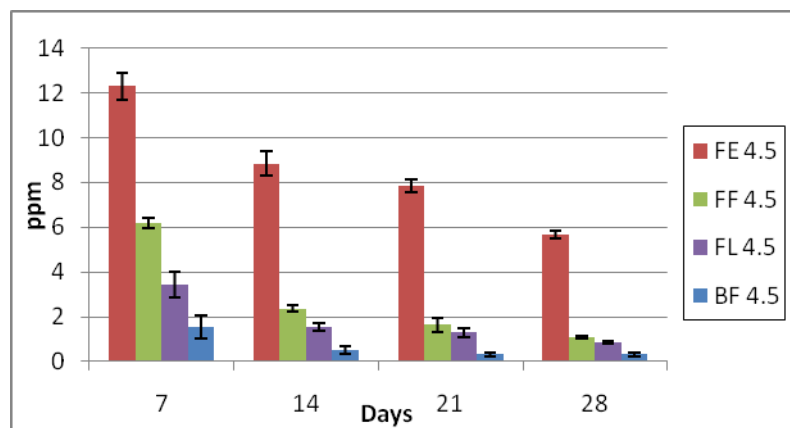
Materials	Before	Week 1	Week 2	Week 3	Week 4
FE	0.03 (0.01)	0.14 (0.03)	0.36 (0.02)	0.52 (0.08)	0.75 (0.06)
FF	0.03 (0.01)	0.13 (0.02)	0.27 (0.02)	0.38 (0.04)	0.55 (0.05)
FL	0.05 (0.01)	0.12 (0.02)	0.19 (0.03)	0.22 (0.02)	0.31 (0.03)
BF	0.05 (0.02)	0.16 (0.02)	0.20 (0.01)	0.23 (0.02)	0.23 (0.02)

Table 5.10: Comparison of surface roughness between different materials (> indicates statistically significant difference and NS indicates no significant difference)

Days	pH 4.5	pH 3.5	pH 2.5
7	FE> BF	FE> FF > FL, BF	NS
14	FE> FL, BF	FE, FF > FL , BF	FE> FF > FL, BF
21	FE> FL, BF	FE, FF> FL> BF	FE> FF, FL, BF
28	FE> FF>FL> BF	FE> FF> FL> BF	FE> FF> FL> BF

Table 5.11: Comparison of surface roughness between different acidic pHs (> indicates statistically significant difference and NS indicates no significant difference)

Days	FE	FF	FL	BF
7	NS	3.5 > 2.5	2.5 > 3.5, 4.5	2.5 > 3.5, 4.5
14	2.5 > 3.5>4.5	2.5, 3.5 > 4.5	2.5 > 3.5, 4.5	2.5 > 3.5, 4.5
21	2.5, 3.5 > 4.5	2.5, 3.5 > 4.5	2.5, 3.5 > 4.5	2.5> 3.5> 4.5
28	2.5> 3.5> 4.5	2.5> 3.5> 4.5	2.5> 3.5> 4.5	2.5> 3.5> 4.5

Fig 5.1: Mean amount of fluoride release from FE, FF, FL and BF for pH 2.5**Fig 5.2: Mean amount of fluoride release from FE, FF, FL and BF for pH 3.5****Fig 5.3: Mean amount of fluoride release from FE, FF, FL and BF for pH 4.5**

5.4: Discussion

Due to the increasing popularity of aesthetic dentistry, the demand for tooth coloured restoratives that are durable, antibacterial and cariostatic have increased significantly. Among the tooth coloured restoratives, GIC are popular mainly due to the fluoride its releasing ability. It has been shown that GIC releases more fluoride in an acidic environment and this could contribute to the probable antibacterial and cariostatic action of the cements (Carey *et al.*, 2003; Czarnecka and Nicholson, 2006; De Moor *et al.*, 2005; Hayacibara *et al.*, 2004; Karantakis *et al.*, 2000). Acidic stressors come from not just the biofilm but also the exogenous sources e.g. acidic beverages etc. Many new glass ionomer containing materials are available and studies are required to investigate their fluoride releasing ability in acidic environments and the relationship between fluoride release and physical properties. In this study, we selected a continuum of restoratives ranging from HVGICs to composite resin to explore the ability of materials to withstand low pH and fluoride release associated. Giomer, being a relatively new material was also included as very few studies have been conducted on it.

Several organic acids solutions and food simulating liquids have been used in *in vitro* studies to analyze the fluoride release profiles and degradation of glass ionomer containing cements in an acidic environment (Forss, 1993; Fukazawa *et al.*, 1987; McKenzie *et al.*, 2003; Yap *et al.*, 2000a). It has also been shown that the amount of fluoride released as well as the effect on the physical properties is not only dependent on H⁺ ions concentration but also on the chelating ability of the acid used (Fukazawa *et al.*, 1987; McKenzie *et al.*, 2003). Due to the variation of the acidic mediums and

different protocols employed in earlier studies, it is difficult to analyze and compare the results. In addition acidic solutions do not simulate the oral environment as in mouth, they get diluted with saliva. In this study, the demineralising solution selected was previously used to investigate the fluoride release kinetics during a cariogenic cycle (Hayacibara *et al.*, 2004). In another study, pH cycling using demineralising/remineralising solution was used to determine the physical properties of the restorative materials (Turssi *et al.*, 2002). The demineralising solution was developed by ten Cate to replicate the acidic saliva for studies. The composition and pH of demineralising and remineralising solution are different. Thus it would be difficult to distinguish the results produced by either of these solutions. Fluoride release is higher in demineralising solution than remineralising solution (Freedman and Diefenderfer, 2003). As the objective was to explore the performance of materials in an acidic medium, the only demineralising solution was used to mimic the low pH environment of the oral cavity. The formulation of all the mediums was standardized and the pH was modulated using 1 M HCl. It was used as a standard medium to analyze the effect of pH on the restorative materials. In this study, pH 4.5 represented the critical pH for hydroxyapatite dissolution during cariogenic attack whilst pH 3.5 and 2.5 represent the various ranges of the acidic environment of the oral cavity due to exogenous and endogenous sources e.g. beverages and acid regurgitation. Samples were continuously agitated at slow speed as erosion cycle requires acid attack and simultaneous removal of products from the materials undergoing dissolution (Eisenburger *et al.*, 2003).

Numerous studies have been conducted to study the degradation of dental restoratives in an acidic environment (Bagheri *et al.*, 2007; Fukazawa *et al.*, 1987; Turssi *et al.*,

2002; Yoshida *et al.*, 1998). Glass ionomer cement, due to their acid base nature is more likely to be affected by acidic environment than the resin based materials (Wan Bakar and McIntyre, 2008; Yoshida *et al.*, 1998).

According to the results of this study, the amount of fluoride release from glass ionomer containing cement was found to be higher in the first week (**Fig 5.1-3**), suggesting the possible ‘outburst’ phenomenon as reported earlier in many studies (Gandolfi *et al.*, 2006; Hayacibara *et al.*, 2004). Independent of materials and evaluation periods, the amount of fluoride release increased with decreasing pH. A similar trend was also observed for surface roughness. The surface roughness was found to increase with decreasing pH. For all the materials the highest fluoride released and Ra was generally observed at pH 2.5 (**Table 5.5 and 5.11**). This was in agreement with many previous studies showing that the amount of fluoride released from glass ionomer containing cement increases in low pH (De Moor and Verbeeck, 1998; De Moor *et al.*, 2005; Forss, 1993; Gandolfi *et al.*, 2006). The dissolution of GIC is controlled by the diffusion of ions through the matrix and also by the formation of complexes at the surface due to the presence of H⁺ ions (Fukazawa *et al.*, 1987). The presence of more H⁺ ions in low pH indicates an erosive phenomenon causing disintegration of matrix and leaching of ions. In this study the correlation between fluoride release and Ra was found to be significant and indicates a dissolution phenomenon. The findings were further confirmed by surface roughness data (**Table 5.7-9**). The results were in agreement with the study conducted by Eisenburger *et al* (2003) that found decreasing pH of the same acidic medium caused more erosion and less chelating effect.

The variation of fluoride release among the materials was dependent on the intrinsic content of fluoride and their chemistry. However, the results differed quantitatively as more fluoride was released in acidic medium than deionized water in our earlier study. HVGICs had the highest roughness followed by the RMGIC and giomer. Resin based cements are more resistant to acidic attack than conventional cements (McKenzie *et al.*, 2003; Sales *et al.*, 2003; Wan Bakar and McIntyre, 2008; Yoshida *et al.*, 1998). Conventional GICs were modified using resin as part of the chemistry to produce RMGICs. As the materials set partly by polymerization, a major part of set cement consists of resin matrix with glass particles embedded in it. It is well accepted that the diffusion mechanism of the matrix of RMGICs control the dissolution process (Sales *et al.*, 2003). Results from the current study corroborated this postulation. Turssi and co-workers showed that the dissolution of matrix around the glass particles suggests possible involvement of the siliceous hydrogel layer (Turssi *et al.*, 2002). The possible reason could be due to the water sorption of the matrix, as the nature of matrix not only determines the rate of diffusion but also controls water sorption (McCabe and Rusby, 2004). Stress is induced around the filler particles after the resin matrix absorbs water, which later contributes to stress corrosion that affects the physical properties of the resin materials (Yap *et al.*, 2001). Giomer showed the highest resistance to erosion and least fluoride release among the fluoride containing materials. They are similar to resin composites but include pre-reacted glass ionomer particles for fluoride release. The matrix of the set cement largely comprises of resin and limited polysalt hydrogel is present. Therefore, the material is more resistant to dissolution and less fluoride release is observed than the rest of fluoride containing materials evaluated in this study.

5.5: Conclusions

All the materials underwent degradation at low pH. Fluoride release and surface roughness increases with decreasing pH. Regardless of the pH, the amount of fluoride is dependent of the material type. Similarly, the ability to withstand harsh chemical environment is largely dependent on material's chemistry. Among the glass ionomer containing cements, HVGICs were more prone to degradation than the RMGIC and giomer. Giomer showed better resistance to degradation. Further *in vitro* investigations are required to analyze the bulk properties of the materials in an acidic environment.

Chapter 6: Fluoride recharge profile of glass ionomer based restoratives materials

6.1: Introduction

Glass ionomer consist of ion leachable aluminofluorosilicate glass and polyacrylic acid or its derivatives. The interaction of polycrylic acid with the glass ionomer results in the release of many ions including fluoride. Fluoride in glass was initially added as flux, which later gave the material its unique property of long term fluoride release contributing to its cariostatic ability.

Several studies have concluded that fluoride release contributes to the anti-cariogenic potential of the glass ionomer cements (Attar and Onen, 2002; Forsten, 1991). Secondary caries, which is one of the main reason of replacing old restorations, was reduced with the use of glass ionomer restoratives (Tyas, 1991). The remineralisation and demineralization inhibition potential of glass ionomer had also been proven and was primarily associated with the fluoride release (Ngo *et al.*, 2006). Due to this reason, Glass ionomer is preferred over other materials for Atraumatic restorative treatment (ART), and has clinically shown to remineralise the affected dentine left underneath restorations (Massara *et al.*, 2002). Similarly bacterial count was reduced after placing glass ionomer cement (Duque *et al.*, 2009). In clinical conditions like xerostomia where patients are at high caries risk, the occurrence of secondary caries was reduced using glass ionomer restoratives (De Moor *et al.*, 2009).

The amount of fluoride release is dependent on many extrinsic and intrinsic factors. Regardless of these factors, the initial high release of fluoride invariably decreases

with time (Wiegand *et al.*, 2007). Glass ionomer cements is not only known to release fluoride but also possess the ability to take up fluoride from the surroundings and re-release it (Forsten, 1991). The recharge potential of glass ionomer cement is considered more important than fluoride release alone as the amount reduces with time (Hatibovic-Kofman *et al.*, 1997). The minimum amount of fluoride required clinically to exhibit remineralisation (Creanor *et al.*, 1995) and antibacterial action has yet not been established. Therefore the continuous uptake and re-release of fluoride can potentially enable the materials to act as “Fluoride reservoir” and can provide longer term anti cariogenic ability.

The uptake or recharge potential of restorative materials has been evaluated using different sources. The uptake and re-release phenomenon is not completely understood however many theories have been postulated regarding it. Some studies have concluded it to be merely surface retained and wash off phenomenon (Attar and Onen, 2002; Hatibovic-Kofman *et al.*, 1997), while others have proposed an ion exchange mechanism (Billington *et al.* 1987). Many factors can influence the uptake/re-release of fluoride from the surrounding. The re-released amount of fluoride after recharging was noted to be the highest in the initial 24-48 hours (Attar and Turgut, 2003) . *In vitro* studies have suggested that the permeability of material, form and concentration of the recharge medium (Preston *et al.*, 2003), frequency of exposure (Freedman and Diefenderfer, 2003) viscosity and pH (Diaz-Arnold *et al.*, 1995; Gao *et al.*, 2000) can affect the uptake/ re-release profile of fluoride .

Conventional glass ionomer has shown to re-release more amount of fluoride than other materials after fluoride recharge (Attar and Onen, 2002; Preston *et al.*, 2003). As uptake/re-release can be influenced by material type and/or recharge medium, it is important to elucidate the uptake/re-release capability of newer available materials and influence of the recharge medium so as to achieve maximum benefit of the materials.

The objective of this phase is to determine the fluoride re-release profile of glass ionomer containing restoratives after recharging with various recharge mediums.

6.2: Materials and methods

The fluoride containing restorative materials included in this study were HVGICs (Fuji IX Extra [FE], Fuji IX Fast [FF]), RMGIC (Fuji II LC [FF]) and Giomer (Beautifil II [BF]). The profiles of the materials are listed in **Table 6.1**. Except for BF, the rest of the materials are encapsulated. The recharge mediums are listed in **Table 6.2**.

Table 6.1: Profiles of the materials investigated

Materials	Batch Number	Shade	Manufacturer	Type	Curing method	Clinical Application
Fuji IX Extra (FE)	805141	A2	GC Asia, Japan	HVGIC	Chemical	Restorative
Fuji IX Fast (FF)	8052901	A2	GC Asia, Japan	HVGIC	Chemical	Restorative
Fuji II LC (FL)	907087	A2	GC Asia, Japan	RMGIC	Light	Restorative
Beautifil II (BF)	60984	A2	Shofu, Japan	Giomer	Light	Restorative

Table 6.2: Profiles of the recharged mediums

Recharge Medium	Manufacturer	Expiry date	Fluoride concentration (ppm)
Colgate Total (CT)	Colgate Palmolive, Thailand	09-03-2013	1450
Tooth mousse Plus (TM)	GC, Japan	12-2011	900
NaF Solution (NaF)	-	-	1000

All materials were mixed according to manufacturers' instructions. The mixed materials were injected into cylindrical recess of stainless steel moulds (8.5mm diameter, 1 mm thickness) and covered with cellulose strips. The filled moulds were then kept between two glass slides and hand pressure was applied to extrude excess material and to obtain a smooth surface finish. After the initial setting, excess material was removed using a scalpel. The light cured materials were polymerized using Curing Light 2500 (3M ESPE, Germany) for 40 seconds. The samples were allowed to set at $\pm 37^{\circ}\text{C}$ in 99% humidity simulating oral environment for 24 hours. The individual specimens were suspended with the help of a dental floss in 15 ml of deionized water in polystyrene containers and transferred to shaking incubator having temperature of 37°C at the speed of 40 rpm. The materials were exhausted by changing deionized water weekly for 4 weeks. After 28 days, specimens of each material were randomly divided into three groups (n=6). To observe the fluoride recharge and re-release phenomenon, three different recharge mediums were selected including two commercially available products Tooth mousse plus (GC Asia, Japan) and Colgate Total (Colgate-Palmolive, Thailand) and a laboratory prepared solution

of NaF. All the recharge mediums were mixed with water in a ratio of 1:1 to form slurry. The specimens were then immersed in the recharge mediums and kept in an incubator for 4 mins representing the usual time for tooth brushing and mouth rinsing per day. After the recharging time, the specimens were washed with deionized water for 1 minute to ensure that recharge mediums have been removed. The specimens were then immersed in 15 ml of deionized water and it was changed daily for the next 7 days.

The daily analysis of fluoride from the collected samples was carried out using Combination Ion selective electrode Model 9609 BNWP (Orion Research, Beverly, USA). For the Fluoride ion measurement, the standards were prepared using 100ppm of NaF standard (Orion Research, Beverly, USA). Three point calibration of the meter was carried out using 0.1, 1 and 10 ppm (part per million) of standards prepared from 100ppm of NaF mixed with equal volume of Total ionic strength adjustment buffer TISAB II (Orion Research, Beverly, USA). The slope achieved between -54mV to -60mV was used to carry out the analysis. To analyze the released fluoride ions, equal volumes (5ml) of sample and TISAB II were mixed together and the readings were recorded in ppm (parts per million).

6.3: Results

Table 6.2 shows the mean amount of fluoride released from materials tested in the different pH. The reading “0” represents the amount of fluoride which was below the detection limit of the fluoride electrode i.e. 0.02 ppm. Results of statistical analyses are reflected in **Table 6.3-4**

Univariate GLM showed significant differences among materials ($p < 0.05$), recharge mediums ($p < 0.05$) and evaluation periods ($p < 0.05$). For all the recharge mediums and evaluation time FE re-released the highest amount of fluoride followed by FF, FL and BF. Among the recharge mediums CT showed the highest ability to recharge whereas no difference was found between TM and NaF. For BF, day 1 showed significant difference between CT and TM.

After exposure to CT, FE, FF and FL re-released significantly more fluoride than BF for days 1 and 2. No significant difference in fluoride re-release was observed between FE, FF and FL. From day 3 to 7 a similar pattern was observed as FE re-released the highest amount of fluoride followed by FF, FL and BF. For the recharge medium TM, a generally similar trend was observed. FE, FF and FL generally showed significant difference in fluoride re-release when recharged with NaF solution.

When statistical analysis was performed for materials, generally CT showed highest recharge potential for FE and FF, whereas NaF showed the least. For FL, CT again showed the highest recharge potential. No difference was observed among TM and NaF. For BF, day 1 showed significant difference between CT and TM.

Table 6.3: Mean amount of fluoride re-released from the materials investigated (Standard deviations are given in parenthesis)

Materials	Recharge Mediums	Fluoride re-release (ppm)						
		Day 1	2	3	4	5	6	7
FE	CT	0.45 (0.04)	0.24 (0.04)	0.23 (0.02)	0.21 (0.03)	0.16 (0.01)	0.1 (0.01)	0.06 (0.01)
	TM	0.26 (0.02)	0.22 (0.02)	0.20 (0.02)	0.20 (0.02)	0.14 (0.02)	0.06 (0.01)	0.04 (0.005)
	NaF	0.34 (0.02)	0.23 (0.02)	0.19 (0.03)	0.17 (0.02)	0.13 (0.02)	0.06 (0.02)	0.04 (0.005)
FF	CT	0.36 (0.04)	0.15 (0.01)	0.11 (0.01)	0.09 (0.01)	0.06 (0.01)	0.03 (0.01)	0
	TM	0.20 (0.01)	0.13 (0.01)	0.12 (0.01)	0.06 (0.001)	0.06 (0.002)	0.05 (0.01)	0.03 (0.001)
	NaF	0.26 (0.02)	0.14 (0.01)	0.10 (0.01)	0.07 (0.01)	0.05 (0.01)	0.03 (0.003)	0
FL	CT	0.48 (0.10)	0.25 (0.04)	0.20 (0.01)	0.15 (0.02)	0.10 (0.01)	0.08 (0.01)	0.04 (0.01)
	TM	0.19 (0.02)	0.16 (0.03)	0.15 (0.02)	0.10 (0.01)	0.05 (0.01)	0.04 (0.003)	0
	NaF	0.24 (0.02)	0.16 (0.06)	0.14 (0.01)	0.11 (0.01)	0.06 (0.01)	0.03 (0.01)	0
BF	CT	0.20 (0.05)	0.06 (0.01)	0.04 (0.01)	0.03 (0.002)	0	0	0
	TM	0.10 (0.02)	0.05 (0.01)	0.04 (0.01)	0.03 (0.01)	0	0	0
	NaF	0.15 (0.03)	0.05 (0.01)	0.03 (0.01)	0.03 (0.002)	0	0	0

Table 6.4: Comparison of fluoride re-released from different materials.
(> indicates statistically significant difference and NS indicates no significant difference)

Days	FE	FF	FL	BF
1	CT> NaF> TM	CT>TM, NaF	CT>TM, NaF	CT> TM
2	NS	NS	CT>TM, NaF	NS
3	CT> TM, NaF	TM > NaF	CT>TM, NaF	NS
4	NS	CT>TM, NaF	CT>TM, NaF	NS
5	CT> TM> NaF	CT,TM> NaF	CT>TM, NaF	NS
6	CT> TM> NaF	TM>CT, NaF	CT>TM, NaF	NS
7	CT>TM, NaF	TM>CT, NaF	CT>TM, NaF	NS

Table 6.5: Comparison of fluoride re-released after recharging with different mediums (> indicates statistically significant difference)

Days	CT	TM	NaF
1	FE, FL> FF> BF	FE> FF, FL> BF	FE> FF> FL> BF
2	FE, FL> FF> BF	FE> FL > FF> BF	FE> FF > FL> BF
3	FE> FL> FF> BF	FE> FF , FL > BF	FE> FF> FL> BF
4	FE> FL> FF> BF	FE> FF> FL> BF	FE> FF, FL> BF
5	FE> FL> FF> BF	FE> FF, FL > BF	FE> FF, FL> BF
6	FE> FL> FF > BF	FE> FF> FL> BF	FE> FF, FL> BF
7	FE> FL> FF, BF	FE> FF> FL, BF	FE> FF, FL, BF

6.4: Discussion

The cariostatic ability of glass ionomer containing cements mainly depends on its fluoride release. Glass ionomer cements have shown a gradual decline in the amount of fluoride release with time. This decline of fluoride release can be overcome by the uptake of fluoride from its surroundings. The material can thus act as a potential reservoir of fluoride. Numerous studies have been conducted to analyze the fluoride recharge potential of glass ionomer containing cements (Forsten, 1991; Gao *et al.*, 2000; Rothwell *et al.*, 1998). Various terms like recharge, uptake and re-release have been used in the literature. However re-release is the more appropriate term to describe material's ability to release fluoride after recharge. In order to evaluate the recharge or uptake characteristic the intrinsic amount of fluoride needs to be known to compare it with the extrinsic fluoride uptake.

In this study a wide range of glass ionomer containing materials including HVGICs, RMGIC and Giomer were selected. Three different categories of fluoride containing recharge mediums including tooth paste, tooth mousse and a NaF (laboratory prepared) solution were selected. The availability of higher concentration of fluoride mouth rinse was difficult therefore NaF solution containing 1000 ppm of F⁻ was prepared to represent mouth rinse in this study.

The amount of fluoride re-released was highest in the first few days and gradually tapers off as shown in many previous studies (Gao *et al.*, 2000; Hatibovic-Kofman *et al.*, 1997). The results of our study showed a general trend among the materials. Among the glass ionomer containing materials, FE re-released the highest amount of fluoride. This result is in agreement with the previous studies showing that conventional glass ionomer cements have better recharge potential than composite

resin (Forsten, 1991; Strother *et al.*, 1998). This could be explained as materials containing intrinsic fluoride can take up more fluoride and re-release it higher quantities (Hadley *et al.*, 1999). The result of our study differs with previous several studies showing the potential of RMGICs to be more than conventional cements (Forsten, 1995; Gao and Smales, 2001; Rothwell *et al.*, 1998). These studies compared conventional glass ionomer cements with RMGIC. However our study used two HVGICs. FE contains specialized fluoroaluminosilicate glass capable of releasing more fluoride due to the presence of extra fluoride in the siliceous layer around the glass particles. Among the intrinsic properties, the type of materials and its permeability greatly contributes to recharge potential (Wiegand *et al.*, 2007). As materials contain higher amount of fluoride than the conventional cements, this possibly leads to higher re-release after recharge. The materials are expected to re-release more fluoride if the intrinsic content of fluoride is higher (Hatibovic-Kofman *et al.*, 1997). This is evident from the results of our study as the re-release of fluoride from the materials followed similar pattern of fluoride release as found in our earlier research. This is possibly due to the different chemistry and intrinsic content of fluoride. Another reason could be the different reactivity of materials to external fluoride sources leading to different amount of re-release (Gandolfi *et al.*, 2006). BF released the lowest amount of fluoride among the glass ionomer containing restoratives. So far very limited studies have explored the recharge potential of giomers. Giomer has shown higher recharge potential against compomers and composite resins and this was attributed due to the presence of extensive hydrogel matrix (Itota *et al.*, 2004). In this study the BF showed higher re-release of fluoride

than composite resin but lesser than RMGICs, which has more hydrogel matrix due to its dual setting chemistry.

The oral cavity is exposed to different fluoride sources in the form food, water and dental products. In this study three different recharge mediums were also used. For FE, FF and FL, CT generally showed the highest recharge potential whereas in BF no difference was observed among the three mediums. Fluoride recharge is dependent on many factors including the pH of the medium, viscosity, concentration and exposure time (Freedman and Diefenderfer, 2003; Gao *et al.*, 2000). The viscosity and concentration of CT was more than TM and NaF. This might be the reason of higher recharge potential of CT. This result corroborates with another study showing higher recharge potential of APF gel owing to its higher viscosity (Gao *et al.*, 2000). The fluoride release after recharging was due to surface adsorption which later gets washed off (Diaz-Arnold *et al.*, 1995). A medium which gets adsorbed are more likely to contribute in higher re-release of fluoride. As other factors like pH and exposure times were standardized in this experiment, the viscosity and concentration could be the likely extrinsic factors contributing in the recharge of restorative materials. Interestingly, no significant difference for BF indicates that intrinsic properties like material's chemistry and surface properties also dictates the amount of fluoride uptake and re-release.

6.5: Conclusions

The amount of fluoride re-released varies with the material type and recharge medium used. Materials containing higher content of fluoride are likely to take up more fluoride and re-release to the surroundings. HVGICs showed more re-release of

fluoride than RMGIC and giomer. The amount of fluoride re-release tapers off with time, however as mouth is frequently exposed to fluoride in various forms hence glass ionomer containing materials have the potential to be used as fluoride reservoir system.

Chapter 7: General Conclusion and Future perspectives

7.1: General Conclusions

The study investigated the fluoride release and surface roughness of various glass ionomer containing restorative materials with respect to different environmental factors like early moisture contamination and pH changes in the oral cavity. The study also investigated the recharge capability of different fluoride sources and the re-release ability of the glass ionomer containing restorative materials.

In chapter 4, the effect of early moisture contamination on glass ionomer containing materials was investigated. The specimens were immersed in water after three different maturation times (10 mins, 30 mins and 24 hours). Fluoride release and surface roughness were analyzed using an Ion selective electrode and a profilometer. The results suggested that HVGICs released highest amount of fluoride when exposed early to moisture i.e. 10 mins whereas 24 hours matured specimens released the least amount. Surface roughness was noted to be higher for HVGICs than RMGIC and Giomer. It was concluded that HVGICs releases the highest amount of fluoride but this was at the expense of increased surface roughness. As there was no significant difference observed between 30 mins and 24 hour specimens. Glass ionomer materials should be protected for at least 30 mins with a resin coating before exposure to moisture.

Environment pH can also degrade restorative materials. In Chapter 5, the effect of acidic pH changes on glass ionomer containing materials was investigated. Demineralizing solution with three different pH i.e. 4.5, 3.5 and 2.5 were used and an accelerated testing method was employed. The specimens were matured for 24 hours

to ensure complete setting. With regards to pH changes it was found that the fluoride release and surface roughness of glass ionomer containing materials were dependent on the pH and material's chemistry. The materials with predominantly acid-base setting showed more fluoride release and surface roughness whereas resin based materials showed the least fluoride release and surface roughness. Among the materials, Giomer showed the lowest surface roughness, but released less fluoride compared to the other glass ionomer containing materials. The most detrimental pH was generally found to be 2.5. At this pH the restorative materials released the highest amount of fluoride, which could be favourable in high caries risk patient where the pH is usually low.

In chapter 6, the fluoride recharging capability of restorative materials and several mediums were evaluated to predict the long term fluoride release of glass ionomer restorative materials. Among the materials, the HVGICs i.e. FE and FF re-released the highest amount of fluoride after recharging whereas the highest recharge potential was observed for CT (Colgate Total) medium. Clinically this can be a useful property of materials as sustained release of fluoride from the restorative material is always considered beneficial for the supporting tooth structure.

7.2: Future Perspectives

Within the limitations of the study it was found that HVGICs released the highest amount of fluoride, however, greater surface roughness was also observed. Not much data has been reported regarding the relatively new material i.e. Giomer. The material can be potentially used in high caries risk patients as it showed less surface roughness but with a lower level of fluoride release. Since the minimum of fluoride for caries

inhibition is still unknown, future studies should be carried out to investigate the minimum amount of fluoride required for caries inhibition. In this study, an accelerated *in vitro* method was employed to test the glass ionomer containing materials. For closer simulation of the oral environment, the pH cycling method i.e. demineralising and remineralizing cycles can be utilized to study the properties of these materials. Further microscopic level analyses are required to investigate the actual mechanism of surface degradation and its association with fluoride release.

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Appendix

Preparation of Demineralizing solution

Stock Solutions

- To make 10mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ stock solution, weigh 1.4702g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and dissolve in 1 liter de ionized water.
- To make 10mM KH_2PO_4 stock solution, weigh 1.3609g KH_2PO_4 and dissolve in 1 litre deionized water.
- To make Ten Cate Demineralizing Solution containing 2.20 mM Ca^{2+} , 2.20 mM P_4^{-3} , 0.05 Acetic acid with a pH of 4.5.

In a liter volumetric flask

- Add 220 mls of 10mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ stock solution
- Add 220 mls of 10mM KH_2PO_4 stock solution
- Weigh out 11.184g of KCl and add to a flask.
- Add 2.87 mls of concentrated glacial acetic acid.
- The desired pH of 4.5 is obtained. pH can be adjusted using 1M HCl solution.