CHARACTERIZATION PHYSICO-MECHANICAL AND CHEMICAL PROPERTIES OF NANO-HYDROXYAPATITE-SILICA ADDED GLASS IONOMER CEMENT

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by

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LIST OF ABBREVIATIONS

ADA	American dental association
ANOVA	One-way analysis of variance
ANSI	American national standard institute
ART	Atraumatic restorative technique
ASPA	Alumino-silicate polyacrylic acid
ASTM	American society of testing and materials
BAG	Bio-active glass
BisGMA	Bisphenol A glycidyl methacrylate
Ca/P	Calcium/phosphorus
CEJ	Cemento-enamel junction
CFS	Compressive fracture strength
cGIC	Conventional glass ionomer cement
CHX@pMSN	Chlorhexidine-encapsulated mesoporous silica nano-particles
CIE	Commission internationale de l'eclairage
Corp	Corporation
CR	Composite resin
CS	Compressive strength
CTE	Co-efficient of thermal expansion
DPSC	Dental pulp stem cell
DTS	Diametral tensile strength
EDX	Energy dispersive x-ray
FDA	Food and drug administration

FS	Flexural Strength
FTIR	Fourier transform infra-red
GIC	Glass ionomer cement
GRAS	Generally regarded as safe
HA	Hydroxyapatite
HA/ZrO_2	Hydroxyapatite/zirconia
HEMA	Hydroxyethyl methacrylate
HUSM	Hospital Universiti Sains Malaysia
HV	Hardness value
ICDD	International centre for diffraction data
IEL	Ion-exchange layer
ISE	Ion specific electrode
ISO	International organization for standards
KBr	Potassium bromide
nano-Ag	Nano-silver
Nano-FA	Nano-fluorapatite
nano-HA	Nano-hydroxyapatite
nano-HA-SiO_2	Nano-hydroxyapatite-silica
nano-HA-SiO_2-GIC	Nano-hydroxyapatite-silica-glass ionomer cement
Nano-SiO_2	Nano-silica
Nano-ZrO_2	Nano-zirconia
Nano-Zr-SiO_2-HA	Nano-zirconia-silica-hydroxyapatite
NBS	National bureau of standards
pH	Potential hydrogen

PVC	Polyvinyl chloride
RMGIC	Resin modified glass ionomer cement
rpm	Rounds per minutes
SBS	Shear bond strength
SD	Standard deviation
SEM	Scanning electron microscope
SEM/EDX	Scanning electron microscope/Energy dispersive x-ray
Sol	Solution
TEGDMA	Tri ethylene glycol di methacrylate
TEM	Transmission electron microscope
TEOS	Tetraethyl orthosilicate
TISAB	Total ionic strength adjustment buffer
XRD	X-ray diffraction

LIST OF SYMBOLS

%	Percentage
~	Around
<	Less than
±	Plus, minus
≤	Less than or equals to
α	Level of significance
ß	Power of the study
δ	Difference in population means
Δ E	Colour change
µm	Micrometre
Ag_{+}	Silver ion
Al	Aluminium
Al_2O_3	Alumina
Al^{3+}	Aluminium ion
$AlPO_4$	Aluminium phosphate
B	Breadth
Ba	Barium
Ca	Calcium
$Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite
Ca^{2+}	Calcium ion
CaF_2	Calcium fluoride
CaO	Calcium oxide

CaOH	Calcium Hydroxide
CO_2	Carbon dioxide
D	Diameter
EtOh	Ethanol
F	Force
F	Fluoride
F+	Fluoride ion
G	Gram
Gf	Gram force
H_2O	Water
H_3PO_4	Phosphoric acid
H_4SiO_4	Silicic acid
hkl	Millers indices
Kg	Kilogram
L	Length
La	Lanthanum
M	Mass
Mg	Magnesium
ml	Millilitre
mm	Millimetre
MN	Meganewton
MPa	Mega pascal
ms	millisecond
N	Sample size

Na^+	Sodium ion
Na_2O	Sodium oxide
Na_3AlF_6	Cryolite
NaF	Sodium fluoride
Nb_2O_5	Niobium pentoxide
NH_3	Ammonia
Nm	Nanometre
O	Oxygen
^oC	Degree centigrade
OH	Hydroxide
^oK	Degree kelvin
P	Pressure
P_2O_5	Phosphorus pentoxide
Ra	Surface roughness
S	Second
Si	Silicate
Si^{4+}	Silica ion
SiO_2	Silica
Sr	Strontium
SrO	Strontium oxide
TiO_2	titanium oxide
V	Volume
Wsl	Water solubility
Wsp	Water sorption

Wt	Weight
wt %	Weight percentage
Zn	Zinc
ZnO	Zinc oxide
ZrO_2	Zirconia

PERINCIAN SIFAT FIZIKO-MEKANIKAL DAN SIFAT KIMIA NANO HIDROKSIAPATIT-SILIKA DALAM SIMEN IONOMER KACA NOVEL

ABSTRAK

Tujuan kajian ini adalah untuk mensintesis dan mencirikan zarah nano-hidroksiapatit-silika (nano-HA-SiO_2) dan mengkaji kesan penambahan nano-hidroksiapatit-silika terhadap simen ionomer kaca konvensional (Fuji IX GC). Nano-HA-SiO_2 telah disintesis menggunakan teknik one-pot sol-gel, yang kemudian dicirikan menggunakan "fourier transform infrared spectroscopy" (FTIR), "x-ray diffraction" (XRD), "scanning electron microscopy" (SEM) dan "transmission electron microscopy" (TEM) . Penyiasatan lanjut dilakukan terhadap simen ionomer kaca yang ditambah nano-HA-SiO_2 (nano-HA-SiO_2-GIC), untuk membandingkan sifat mekanikal (kekerasan permukaan, kekuatan mampatan, kekuatan lenturan dan kekuatan ikatan ricih), sifat kimia (pelepasan ion fluoride, kelarutan dan pertukaran ion) dan sifat fizikal (kestabilan warna, kekasaran permukaan, penyerapan dan kebocoran mikro) berbanding dengan simen ionomer kaca konvensional (cGIC). Serbuk nano telah dibuktikan bahawa terdiri daripada campuran zarah silika sfera (~50 nm) dan zarah hidroksiapatit yang memanjang dalam julat antara 100-200 nm. Kekerasan, kekuatan mampatan, dan kekuatan lenturan nano-HA-35SiO_2-GIC didapati lebih tinggi secara statistik berbanding nano-HA-21SiO_2-GIC and nano-HA-11SiO_2-GIC. Nilai tertinggi untuk kekerasan Vickers (64.77 ± 6.18), kekuatan mampatan (143.42 ± 13.94 MPa) dan kekuatan lenturan (17.68 ± 1.81 MPa) direkodkan dengan penambahan 10% nano-HA-35SiO2 kepada GIC. Ianya telah meningkatkan kekerasan permukaan, kekuatan mampatan dan kekuatan lenturan masing-masing sebanyak ~36%, ~19.7% dan ~53.34% jika dibandingkan dengan simen ionomer

kaca konvensional (cGIC). 10% nano-HA-35SiO_2-GIC juga menunjukkan kekuatan ikatan ricih yang tinggi (peningkatan ~17.54%) berbanding dengan cGIC. Nano-HA-35SiO_2-GIC adalah bahan yang lebih stabil warna kerana ia dilaporkan menglami perubahan "slight - noticeable" warna berbanding dengan cGIC yang menunjukkan perubahan "noticeable - appreciable" warna selepas rendaman dalam air suling selama 28 hari. Nano-HA-35SiO_2-GIC dilaporkan mempunyai kekasaran permukaan yang rendah (0.13 ± 0.01 μm) lebih ketara berbanding cGIC (0.16 ± 0.03 μm) pada hari pertama. Selain itu, nano-HA-35SiO_2-GIC juga dilaporkan perbezaan yang besar ($p=0.002$) dalam min/purata jumlah F^+ dibebaskan untuk semua selang/jarak masa berbanding dengan cGIC ($p \leq 0.05$). Di samping itu, Nano-HA-35SiO_2-GIC mencatatkan nilai yang lebih tinggi untuk kelarutan dan penyerapan (83.7 ± 19.04 μgmm^{-3} dan 50.92 ± 12 μgmm^{-3}) berbanding cGIC (56.65 ± 10.15 μgmm^{-3} dan 42.64 ± 6.74 μgmm^{-3}). Ia juga menunjukkan kebocoran mikro yang lebih rendah pada hujung oklusal dan gingival (0.2 ± 0.42 dan 2.7 ± 0.67) berbanding dengan cGIC (0.5 ± 0.71 dan 3 ± 0.00). Pertukaran ion yang lebih tinggi telah ditunjukkan oleh nano-HA-35SiO2-GIC pada lapisan pertukaran ion (IEL) serta struktur gigi (enamel dan dentin) berbanding dengan cGIC. Penambahan nano-hidroksiapatit-silika kepada GIC konvensional telah meningkatkan sifat mekanikal, fizikal dan kimia kecuali sifat penyerapan bahan. Berdasarkan penemuan yang kajian semasa, nano-HA-SiO_2-GIC boleh dicadangkan sebagai bahan tampalan pergigian yang berpotensi dalam bidang pergigian.

CHARACTERIZATION PHYSICO-MECHANICAL AND CHEMICAL PROPERTIES OF NANO-HYDROXYAPATITE-SILICA ADDED GLASS IONOMER CEMENT

ABSTRACT

The aim of this study was to synthesize and characterize different nano-hydroxyapatite-silica (nano-HA-SiO_2) particles with various silica concentrations and to investigate the effects of adding nano-HA-SiO_2 to the conventional glass ionomer cement (Fuji IX GC). Nano-HA-SiO_2 was synthesized using one-pot sol-gel technique, which was then characterized using fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). Further investigations were carried out on nano-HA-SiO_2 added glass ionomer cement (nano-HA-SiO_2-GIC) to compare their mechanical (surface hardness, compressive strength, flexural strength, and shear bond strength), chemical (fluoride ion release, solubility and ion-exchange) and physical properties (colour stability, surface roughness, sorption and micro-leakage) in relation to conventional glass ionomer cement (cGIC). It was found that nano-powder consisted of a mixture of spherical silica particles (~50 nm) and elongated hydroxyapatite particles in the range between 100-200 nm. Hardness, compressive strength, and flexural strength of nano-HA-35SiO_2-GIC was statistically higher than that of nano-HA–21SiO_2–GIC, nano-HA-11SiO_2-GIC. The highest value for Vickers hardness (64.77 ± 6.18), compressive strength (143.42 ± 13.94 MPa) and flexural strength (17.68 ± 1.81 MPa) were recorded by addition of 10% nano-HA-35SiO_2 to GIC, leading to an increase of ~36 %, ~19.7 % and ~53.34 % in surface hardness, compressive strength and flexural strength respectively as compared to conventional glass ionomer

cement (cGIC). 10% nano-HA–35SiO_2-GIC also demonstrated higher shear bond strength (~17.54 % increase) as compared to cGIC. Nano-HA-35SiO_2-GIC was more colour stable material as it showed "slight - noticeable" change in colour as compared to cGIC that displayed "noticeable to appreciable" change after 28 days of immersion in distilled water. Nano-HA-35SiO_2-GIC showed significantly lower surface roughness (0.13 ± 0.01 μm) as compared to cGIC (0.16 ± 0.03 μm) on day 1. Additionally, nano-HA-35SiO_2-GIC showed highly significant difference (p=0.002) in amount of mean F^+ release for all the time intervals as compared to cGIC ($p \leq 0.05$). In addition, Nano-HA-35SiO_2-GIC recorded higher values for both solubility and sorption (83.7 ± 19.04 μgmm^{-3} and 50.92 ± 12 μgmm-3) as compared to cGIC (56.65 ± 10.15 μgmm^{-3} and 42.64 ± 6.74 μgmm^{-3}). It also exhibited lower micro-leakage both at occlusal and gingival margins (0.2 ± 0.42 and 2.7 ± 0.67) as compared to cGIC (0.5 ± 0.71 and 3 ± 0.00). A greater ion-exchange was displayed by nano-HA-35SiO_2-GIC at ion-exchange layer (IEL) as well as the tooth structure (enamel and dentin) as compared to cGIC. The addition of nano-HA-silica to conventional GIC significantly enhanced the mechanical, physical and chemical properties except sol-sorption properties of the material. Based on the findings of the current study, nano-HA-SiO_2-GIC can be suggested as a potential dental restorative material.

CHAPTER 1

INTRODUCTION

1.1 Background

Glass ionomer cement (GIC) which was previously referred to as "glass polyalkenoate" is a remarkable biocompatible dental restorative material used for multiple clinical applications. It is a tooth-coloured restorative material (Craig, 2002), created by Wilson *et al*. in 1969 (Wilson and Kent, 1972). This material is based on an acid-base chemical reaction between alumino-silicate glass powder and polyacrylic acid (Wilson and Nicholson, 1993). Therefore, they are known as water-based cement (Crisp *et al.*, 1975a). GIC is a tooth-coloured (Wilson, 1996), translucent material (Nicholson, 2010) and is adhesive to natural tooth structure (Van Meerbeek *et al.*, 2003; Yoshida *et al.*, 2000). Other properties which help GIC in gaining its popularity in clinical practice are its good biocompatibility (Sidhu and Schmalz, 2001), along with fluoride release (Lee *et al.*, 2000) and coefficient of thermal expansion value close to that of the natural tooth (Moshaverinia *et al.*, 2008a). Based upon these properties, GIC has a vast variety of clinical application such as filling material for paediatric patients, used in atraumatic restorative techniques (ART), sandwich technique, as pits and fissure sealant, lining material, core build-up material, luting cement for crown, bridges and veneers and repair of defective margins (Moshaverinia *et al.*, 2011).

Despite those advantages, GIC has low mechanical properties. It is brittle and mechanically weak (Nicholson, 2010), therefore, limiting its clinical usage (Berg and Croll, 2015). Since its inception, there have been many attempts to overcome their weak mechanical properties

by modifying the glass ionomer cement powder and liquid. This include integration of reinforcing phase such as N-vinylpyrrolidone (Moshaverinia *et al.*, 2009), strontium oxide (Deb and Nicholson, 1999), stainless steel (Kerby and Bleiholder, 1991), hydroxyapatite (Choudhary and Nandlal, 2015), zirconia (Gu *et al.*, 2005c), zinc (Zoergiebel and Ilie, 2013), titanium (Garcia-Contreras *et al.*, 2015), silica (Felemban and Ebrahim, 2016), and fibre-reinforcement (Lohbauer *et al.*, 2003b). These attempts have been aimed to improve the mechanical, physical and bonding properties of glass ionomer cement.

Micron-sized hydroxyapatite (HA) (Gu *et al.*, 2005a) and silica (SiO_2) (Felemban and Ebrahim, 2016) have been used as fillers for GIC which has exhibited better mechanical properties as compared to conventional GIC. It has been reported in the literature that incorporation of fillers or re-enforcing agents in the glass ionomer cement matrix can prevent the crack propagation in the resin matrix, thus enhancing the mechanical properties of the material (Arita *et al.*, 2011; Rahman *et al.*, 2014). In addition, beneficial results has been reported with regards to anti-bacterial efficacy, fluoride release and surface roughness with the addition of nano-particles by several authors (Elgamily *et al.*, 2018; Lopes *et al.*, 2018; Moshaverinia *et al.*, 2008a). This, in turn, would make glass ionomer cement to become one of the choices of material for posterior load-bearing restorations.

These days, the use of nano-fillers is becoming popular as they have demonstrated superior mechanical properties in comparison to conventional GIC (Najeeb *et al.*, 2016). Nano-hydroxyapatite (nano-HA) has a similar chemistry to dental hard tissues. For this reason, they have been used quite frequently as a filler in restorative materials. It has been shown that addition of nano-HA increases the crystallinity of the set GIC (Moshaverinia *et al.*, 2008a).

Apart from enhancing the mechanical properties, it provides a positive atmosphere for remineralization of enamel (Huang *et al.*, 2011; Moshaverinia *et al.*, 2008a). Similarly, there has been an increased interest in the use of nano-silica (nano-SiO_2) as an additive to GIC (Mabrouk, 2012). It was reported that the addition of nano-SiO_2 to GIC boosts its bioactivity which could lead to prevention of marginal gap formation inside the tooth (Mabrouk, 2012).

Rahman *et al.* (2014) has for the first time, used the combination of nano-HA and nano-SiO_2 i.e nano-hydroxyapatite-silica (nano-HA-SiO_2) as a filler for GIC. It was demonstrated that the addition of nano-HA-SiO_2 increases the hardness value of the tested material as compared to the use of conventional GIC alone (Rahman *et al.*, 2014). They suggested that these favourable findings could be related to an increased packing density as a result of nano-silica particles filling the voids between the nano-HA in GIC matrix (Rahman *et al.*, 2014). They found that nano-HA crystals were elongated in shape while the nano-SiO_2 particles were smaller and spherical in shape. On top of that, cytotoxicity evaluation of the same material has been carried out on human dental pulp stem cells (DPSC). It was reported that nano-hydroxyapatite-silica-Glass ionomer cement (nano-HA-SiO_2-GIC) demonstrated favourable cytotoxic response as well as maintaining the spindle morphology of human DPSC's (Noorani *et al.*, 2017).

However, in order to suggest nano-HA-SiO_2 to be an additive filler to glass ionomer cement powder, further investigations are required. In the current study, Nano-hydroxyapatite-silica powder was synthesized utilizing the one pot sol-gel technique with one modification, which involved modifying the mixing method. In this instance, magnetic mixing and mechanical mixing methods were used for the current study. It is postulated that these different mixing

techniques might influence the shape and size of the nano-particles synthesized, which in turn might affect the properties of the synthesized composite material.

1.2 Problem statement

Currently, most of the commercially available GIC fulfil the minimum criteria of ISO standard 9917-1 and are categorized as clinical grade GIC (ISO, 2003). To overcome the weakness of cGIC, metal particles such as silver and gold as re-enforcing agents have been used (McLean and Gasser, 1985). The addition of metal particles resulted in an increase in strength of GIC, but compromising the aesthetics, tooth adhesion and fluoride release of the material. Addition of micron-sized zirconia and glass fillers has also been reported with a slight increase in mechanical properties (Gu *et al.*, 2005a; Gu *et al.*, 2005b). However, these improvements were not very significant. Most likely the reason for this could be the micron-size of the fillers used. Lopes *et al*. (2018) experimented on HA added GIC and reported an increase in the surface roughness (Ra) value (0.20 ± 0.07 μm) of the tested material. An increase in surface roughness could lead to an increase in microbial adhesion, plaque accumulation and thus could lead to increased risk of caries and periodontal disease (Bollen *et al.*, 1997). Experimental nano-HA-SiO_2 was added to GIC and it was reported that the material has better surface hardness and favourable toxic response (Noorani *et al.*, 2017; Rahman *et al.*, 2014). Nonetheless, there is no detailed work available on the addition of nano-HA-SiO_2 to GIC with regards to its mechanical properties such as surface hardness, compressive, flexural and shear bond strength. In addition, physical and chemical properties of nano-HA-SiO_2-GIC with regards to colour stability, surface roughness, sorption, microleakage, fluoride release, solubility and ion-exchange are yet to be reported. Moreover,

there is a lack of data on the comparison of effect of different mixing techniques on the synthesized nano-HA-SiO_2 powder by one pot sol-gel technique. It has been suggested that different mixing methods for synthesising nano-powder might produce a material with different characteristics of nano-HA-SiO_2. In this case, several scientists have reported different characteristics for nano-particles (nano-SiO_2 and nano-HA) produced with different synthesis techniques (Rahman *et al.*, 2017; Rahman *et al.*, 2014; Rahman and Padavettan, 2012; Yazdimamaghani *et al.*, 2013).

1.3 Justification of the Study

Nowadays, GIC is one of the most widely used restorative materials that is being employed by dentist worldwide both in urban and rural setup (Tyas, 2018). It is particularly utilized in Atraumatic Restorative Treatment (ART) for high caries risk patients (Yip *et al.*, 2001a). Historically, cGICs are mechanically weak and thus are not indicated for restoring stress-bearing areas inside the oral cavity (Prakki *et al.*, 2005; Yip *et al.*, 2001a). Ideally, the ART requires a material with enhanced mechanical properties and bonding ability. Various types of GICs have been purposely formulated for ART restorations. Many i*n-vitro* studies have compared the performance of cGICs to high-density GICs and filler modified GIC (Hussin *et al.*, 2018; Lucas *et al.*, 2003; Moshaverinia *et al.*, 2008a; Nishimura *et al.*, 2014; Panahandeh *et al.*, 2018; Prakki *et al.*, 2005; Yip *et al.*, 2001a). They found out that it still lacks the performance required as a universal restorative material.

The basic concept behind the current study is to synthesize nano-HA-SiO_2 with varying amount of silica concentration that will be added as a re-enforcing agent for the conventional

glass ionomer cement. This incorporation of nano-hydroxyapatite-silica to glass ionomer cement might alter the properties of GIC, thus making conventional glass ionomer cement a better restorative material mechanically, physically and chemically. In addition, diffusion of ions at the nano-hydroxyapatite-silica-GIC enamel/dentine interfaces might enhance the bonding characteristics of glass ionomer cement to the tooth. To the best of our knowledge, studies that report an effect of addition of nano-HA-SiO_2 to GIC on mechanical properties such as surface hardness, compressive, flexural and shear bond strength is yet to be reported. In addition, physical and chemical properties of nano-HA-SiO_2-GIC with regards to colour stability, surface roughness, sorption, microleakage, fluoride release, solubility and ion-exchange are yet to be determined.

Therefore, the novel findings of the current study will have the potential to expand the future application of GIC in clinical practice both in urban and rural setup, thus paving the way for a wider application of GIC in restorative dentistry.

1.4 General Objective

To synthesize and characterize novel nano-hydroxyapatite-silica added restorative material based on glass ionomer cement for dental applications and compare it with conventional glass ionomer cement.

1.5 Specific Objectives

1. To synthesize and characterize different compositions of nano-hydroxyapatite-silica powder containing various silica concentration by using fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM).
2. To synthesize and characterize nano-hydroxyapatite-silica powder using a one-pot sol-gel method, with various mixing techniques using SEM, FTIR and XRD.
3. To synthesize and characterize nano-hydroxyapatite-silica-glass ionomer cement using FTIR and SEM-dot mapping.
4. To evaluate and compare the mechanical properties of nano-hydroxyapatite-silica-GIC with conventional glass ionomer cement in terms of surface hardness, compressive strength, flexural strength and shear bond strength.
5. To evaluate and compare the physical properties of nano-hydroxyapatite-silica-GIC with conventional glass ionomer cement in terms of colour stability, surface roughness, sorption and microleakage.
6. To evaluate and compare the chemical properties of nano-hydroxyapatite-silica-GIC with conventional glass ionomer cement in terms of fluoride release, solubility and ionic-exchange.

1.6 Research questions

- Can nano-hydroxyapatite-silica particles with various silica composition be successfully fabricated through one-pot sol-gel method?

- Can nano-hydroxyapatite-silica particle with different morphology be produced when using different mixing techniques during one-pot sol-gel synthesis method?
- Can nano-hydroxyapatite-silica particles be successfully incorporated in glass ionomer cement?
- Does addition of nano-hydroxyapatite-silica particle enhance the mechanical properties of GIC compared with conventional glass ionomer cement in terms of surface hardness, compressive strength, flexural strength and shear bond strength?
- Does addition of nano-hydroxyapatite-silica particle enhance the physical properties of GIC compared with conventional glass ionomer cement in terms of colour stability, surface roughness, sorption and micro-leakage?
- Does addition of nano-hydroxyapatite-silica particle enhance the physical properties of nano-hydroxyapatite-silica-GIC compared with conventional glass ionomer cement in terms of fluoride release, solubility and ion-exchange?

1.7 Research hypotheses

- Different compositions of nano-hydroxyapatite-silica powder containing various silica concentration can be successfully synthesized via one-pot sol-gel method.
- Nano-hydroxyapatite-silica particles with different morphologies can be synthesized with different mixing techniques synthesized via one-pot sol-gel method.
- Nano-hydroxyapatite-silica particles can be successfully incorporated into glass ionomer cement.

- The addition of nano-hydroxyapatite-silica powder to conventional GIC enhances the mechanical properties of GIC in terms of surface hardness, compressive strength, flexural strength and shear bond strength.
- The addition of nano-hydroxyapatite-silica powder to conventional GIC enhances the physical properties of GIC in terms of colour stability, surface roughness, water sorption and microleakage.
- The addition of nano-hydroxyapatite-silica powder to conventional GIC enhances the chemical properties of GIC in terms of fluoride release, solubilty and ionic-exchange.

1.8 Research Summary

The new material was synthesized by adding nano-HA-SiO_2 powder to conventional glass ionomer cement (cGIC) powder and mixed with the conventional glass ionomer liquid. The nano-HA-SiO_2 powder and nano-HA-SiO_2 glass ionomer cement (nano-HA-SiO_2-GIC) were investigated by scanning electron microscope (SEM), transmission electron microscope (TEM), x-ray diffraction (XRD) and fourier transform infrared microscope (FTIR). Following characterization of the powder, the nano-HA-SiO_2-GIC was then evaluated for surface hardness, compressive strength, flexural strength, shear bond strength, color stability, surface roughness, micro-leakage, fluoride release, sol-sorption and ion-exchange. The newly developed nano-HA-SiO_2-GIC were compared with the commonly available commercial type of conventional glass ionomer cement; GC Fuji IX (Japan). All the tests were carried out in accordance with the International Standard Organization (ISO) standards; ISO 9917-1 (dentistry – water-based cements), ISO 11405 (testing of adhesion to tooth structure), ISO 4049 (dentistry - polymer-based restorative materials) ISO 19448 (dentistry

- analysis of fluoride concentration in aqueous solutions by use of fluoride ion-selective electrode) and ISO 7491 (dental materials - determination of color stability).

The flow chart showing outline of the current study is presented in Figure 1.1.

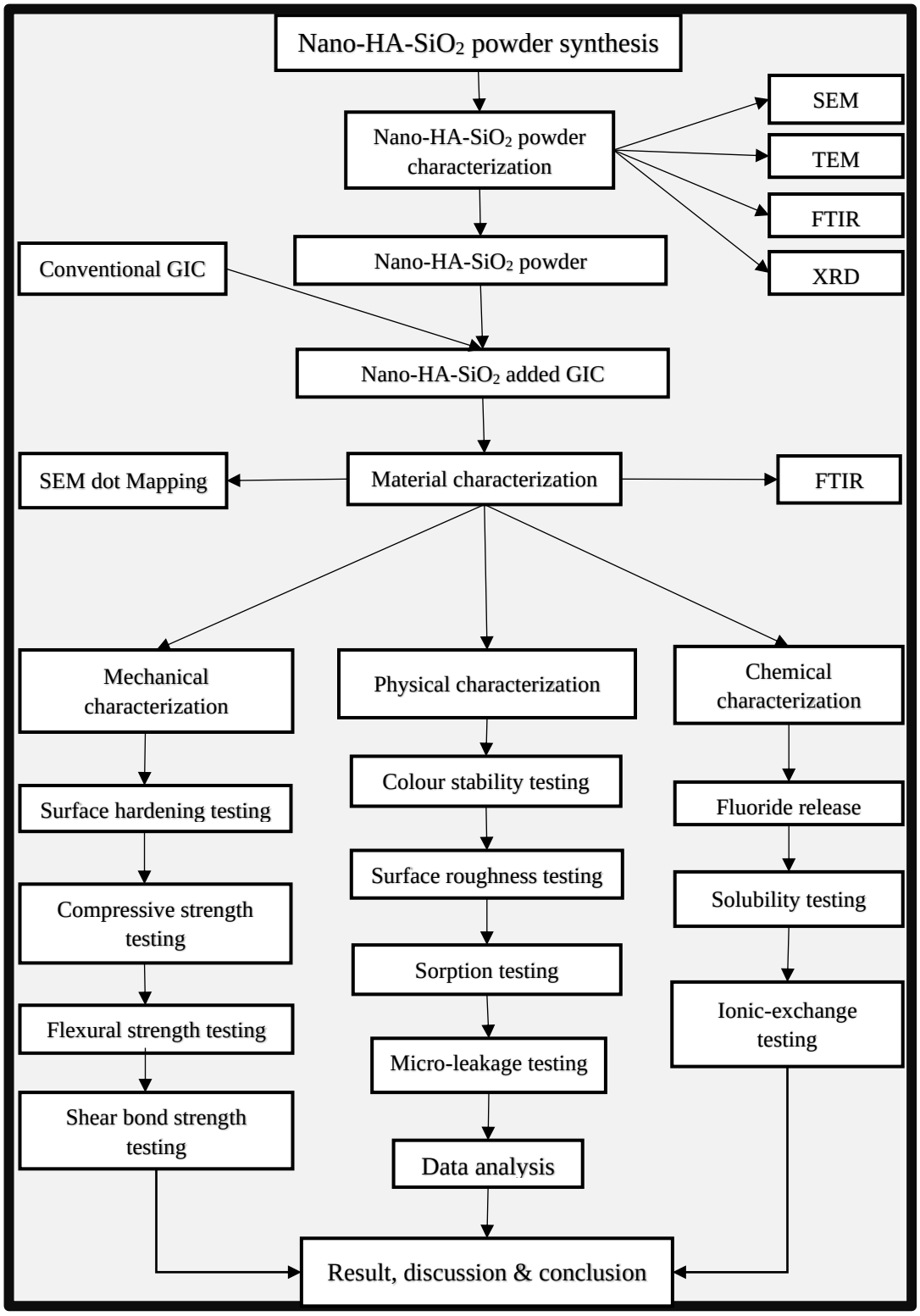

Figure 1.1: Flowchart of research methodology

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The science of dental material includes philosophy of dealing with materials belonging to two major subdivisions of dentistry; restorative dentistry and prosthodontic dentistry (McCabe and Walls, 2013). The science of dental materials is one the basic and main branch of dentistry that deals with topics like amalgam alloys, glass ionomer cements, dental composites, dental waxes, dental impression materials, denture base materials, ceramics, gypsum compounds, noble and cast metals and various materials used for surgical, clinical and lab procedures. The characterization of these materials is generally done on the basis of chemistry, mechanical, physical, chemical and biological properties. Thus, dental materials should be studied from a point of view that determines the composition of the material, how it functions under mechanical, physical and chemical challenges and how it can be modified to function according to the desired requirement. Dental materials are used in most of the branches of dentistry and there is hardly any dental clinical procedure, which does not involve the application of a dental material. The application of dental materials is not only limited to dentistry as some of the dental materials are finding its way in the medical science for cases such as bone fracture and bone replacement.

2.2 History of glass ionomer cement

Glass ionomer cements were developed in the 1960s by Alan Wilson and his team of co-workers as a replacement to dental silicate cements (Wilson and Kent, 1972). Before the

advent of glass ionomer cement, dental silicate cements were the first choice of aesthetic restorative material for anterior teeth. Dental silicate cements possessed a number of undesirable characteristics. They did not bond to natural tooth structures, they were prone to acid erosion, they were brittle in nature and they were prone to cause pulpal sensitivity (Wilson and Batchelor, 1967a). A major obstacle in the evolution of dental silicate cements were the dearth of knowledge regarding the mechanism of setting chemistry of these cements (Wilson, 1996).

Wilson and Batchelor (1967b) made a breakthrough discovery in understanding the setting chemistry of the cement. For the betterment of the cement, experiments were performed by Wilson and co-workers on different series of acids like pyruvic, tartaric, tannic, fluoroboric, glycerophosphoric, tetraphosphoric and acrylic acid. These acids were used at different concentration in solution with the aluminosilicate glass (Wilson, 1968). The cement produced as a result had slow setting time with reasonable working and handling time (Wilson, 1968). However, the cement formed as a result of addition of polyacrylic acid solution reported reduced vulnerability to hydrolytic breakdown but had "little or no working time" (Wilson, 1996).

Wilson and Kent (1972) discovered that the reactivity of the glass particles in the cement was controlled by adjusting the alumina : silica ratio, whereby novel glass compositions were used to produce a hydrolytically stable cement by Wilson and Kent (1972). This cement was first reported as the alumino silicate polyacrylic acid (ASPA) cement (Wilson and Kent, 1972). Despite the high expectation for the clinical success of glass ionomer cement (GIC),

the first batch of cement produced was unsuccessful to amaze since it had poor setting characteristics and inadequate working time (Wilson, 1996). As a result of delayed hardening, the earliest GIC were prone to harmful effects moisture contamination and desiccation during initial phase of setting reaction (Causton, 1981; Earl *et al.*, 1989; Wilson, 1989). In an endeavour to enhance the setting characteristics of GICs, Wilson *et al.* (1976) experimented with the composition of the cement by incorporating chelating agents. The chelating agents added for the modification of the setting reaction were citric acid, salicylic acid, acetylene, sequestric acid, polyglycol and tartaric acid. The most promising results were obtained by the addition of tartaric acid (Wilson *et al.*, 1976) and proved to be effective beyond all expectations (Wilson, 1996; Wilson *et al.*, 1976). Addition of tartaric acid produced multiple benefits. It enhanced the working time (Wilson *et al.*, 1976), reduced the setting time (Crisp *et al.*, 1979; Crisp and Wilson, 1976), improved the compressive fracture strength (CFS) (Crisp *et al.*, 1979) and made the GIC more resistant to acid dissolution (Wilson, 1996).

More recently, GIC was modified by introducing a resin into the matrix of conventional GIC producing a newer category of material termed as resin-modified glass ionomer cement (RMGIC) (Wilson, 1990). Synthesizing RMGIC requires a part of the water content was removed from the original composition and was replaced with monomers such as polyethylene glycol and hydroxylethyl methacrylate (HEMA). By introducing these monomers, a hybrid material was produced possessing acid base reaction of the glass component with the polyacid as well as crosslinking of the polyethylene and HEMA. This resulted in material having dual setting characteristic. Resin-modified glass ionomer cement

has a matrix of interpenetrating poly-acid and glass component with crosslinking polymers of the newly added monomers. Resin-modified glass ionomer cement thus produced, retained all the properties of the conventional GIC and acquired better setting characteristics with enhanced flexural strength and toughness (Avila *et al.*, 1996; Culbertson, 2001; Gordan *et al.*, 1998; McCabe and Walls, 2013; Sidhu, 2015; Wilson, 1990). Initial RMGIC were still faced with few shortcomings like material shrinkage upon setting as well as having limited depth of cure (Avila *et al.*, 1996; Blunck *et al.*, 1996; McCabe and Walls, 2013; Sidhu, 2015).

In recent times, a wide range of commercial hand mixed and encapsulated GICs are available to be used by the general dental practitioner in a clinical setting. They are used in different modes for the restoration of anterior and posterior dentition. Glass ionomer cement are classically dispensed in two presentational forms: one, as a separate glass powder and polyacid liquid composition (Wilson and Kent, 1972). Secondly as an anhydrous form that is a mixture of glass powder and vacuum-dried polyacid that is mixed with distilled water or a solution of tartaric acid (McLean *et al.*, 1984; Prosser *et al.*, 1984). Various formulations have been currently used by the manufacturers to modify the handling characteristics and the mechanical properties of GIC by optimizing the glass powder and polyacid constituents. In the current study conventional GIC Fuji IX was selected as the base/control material for the current study because it is the most commonly used material in restorative dentistry. World Health Organization has also recommended GIC Fuji IX as the material of choice for atraumatic restorative treatment (ART) because of its ease of availability and requires no additional complex setup for its setting application (Choudhary and Nandlal, 2015).

2.3 Composition of glass ionomer cement

An ionomer is a reversible crosslinking polymer with ionic groups having tendency to lose their attractions when heated. Ionic repeating units affect polymer properties. Glass ionomers cements used as restorative materials in dental applications, can be self-curing (conventional) or resin-modified (Craig, 2002; Emmott, 2011). Glass ionomer cement has two main ingredients in its composition that are essential to maintain its desirable properties which include polymeric water-soluble acid and ion-leachable glass. These ingredients form a paste, when this fine glass power is mixed with the polymeric acid. Glass ionomers cement sets within 3 minutes after mixing as a result of acid-base reaction between the polyacid and the glass particles. The ions Na^{+} and Ca^{2+} ions move from the glass into the acidic solution where they interact with polyacid molecules forming crosslinks that results in setting of the cement (Emmott, 2011). There are other variations in the composition and dispensation of GIC, such as water and acid are in powdered form that are mixed with water and dilute acid solution to form a blend of acid and glass powder for the setting. These variations do not cause any significant changes in the material properties. The mixing of the cement is usually done with a spatula on a glass block using hands. Glass ionomer cement may also be dispensed inside the bespoke capsule, in which the powder and liquid are separated by a thin membrane. This type of dispensation requires automatic mechanical mixing. Paste formed as a result of this mechanical mixing is removed from the capsule. It is this paste which is used in dentistry for intra-oral application (Emmott, 2011; Voruganti, 2008).

2.3.1 Chemical composition of GIC powder

Glass ionomer cements are composed of an ion-leachable glass powder. Aluminosilicate glass is used to prepare the GIC powder, which provides a constant source of metal ions for the cement forming reaction (Nicholson, 1998). Setting rate of the chemical reaction is controlled by the composition of the glass particles (Kent *et al.*, 1979; Wilson and Nicholson, 1993). Glasses used in the glass ionomer cement are complex and has three major components including silica (SiO_2), alumina (Al_2O_3), calcium fluoride (CaF_2). Mixture of silica and alumina powder are sintered together to produce the glass component. Figure 2.1 shows the basic components of the inorganic glass powder. It also contains sodium fluoride (NaF) and cryolite (Na_3AlF_6) or aluminium phosphate ($AlPO_4$) (Culbertson, 2001; Lohbauer, 2010). The addition of phosphates and fluoride in the glass composition is to control and modify the setting characteristics (Moshaverinia *et al.*, 2011). Alumina and silica are the two main components of the GIC powder, which form the "backbone and skeletal structure of the glass" (Culbertson, 2001).

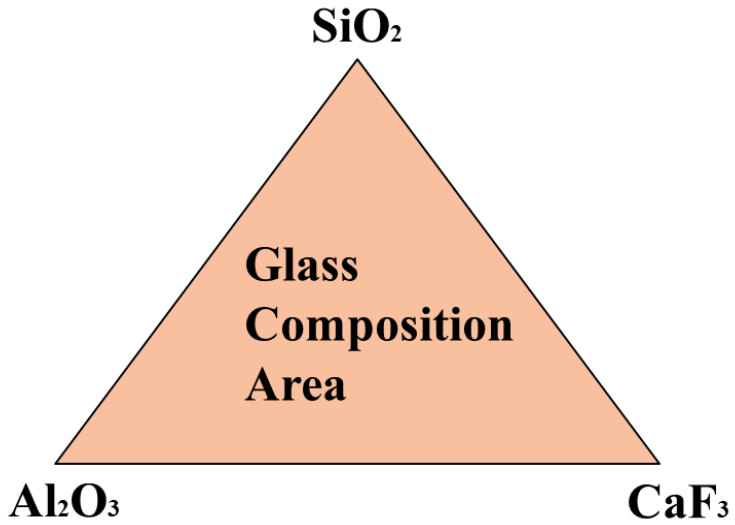

Figure 2.1: Glass-ionomer glass powder composition adapted from Culbertson (2001) (with permission).

The Al:Si ratio and Ca:Al mole ratio in the glass determines the final set cement properties. With Al:Si ratio < 1:1 and Ca:Al mole ratio > 1:2, aluminium is in four-fold coordination while with Al:Si ratio < 1:1 and Ca:Al ratio < 1:2, some ions can take six fold coordination (Cheng *et al.*, 2005; Lohbauer, 2010; Moshaverinia *et al.*, 2011; Nicholson, 1998; Wilson and Kent, 1972). These oxygen linkages are vulnerable to attacks from acids as aluminium ion ($Al^{3+)}$ is weaker than silica (Si^{4+}) ion in its field strength. With F^- ions added, cation bonds are strengthened and thus, linkages are less susceptible to acid attacks (Lohbauer, 2010; Moshaverinia *et al.*, 2011). In the following table Table 2.1 showed chemical composition of the powder component of two early produced GICs which were commercially.

Table 2.1: Powder composition of two different kinds of glass ionomer cements (Wilson and Mclean (1988a)

Components	A (wt %)	B (wt %)
SiO_2	41.9	35.2
Al_2O_3	28.6	20.1
CaF_2	15.7	20.1
NaF	9.3	3.6
$AlPO_4$	3.8	12.0
Na_3AlF_6	1.6	2.4

Every component of GIC plays a significant part in the cement matrix. Aluminium ions protect the cements from acid. Meanwhile sodium ion (Na^+) will contribute towards the

hydrolytic stability of the cement during the setting reaction. Fluoride ion decreases the glass susceptibility towards the acid attack, provides anti-cariogenic properties, improves translucency as well as reduces GIC setting time (Culbertson, 2001). Furthermore, other elements such as Lanthanum (La), strontium (Sr), barium (Ba) or zinc oxide (ZnO) are added in the powder component of GIC to adjust the radio opacity of the set cement (Baig and Fleming, 2015; Lohbauer, 2010; Sidhu, 2011).

2.3.2 Chemical composition of GIC liquid

The second component of the GIC is the liquid which contains polyacids also known as polyalkenoics. The early formulations of GIC contained about 40 – 50 % of aqueous solution of acrylic acid (Moshaverinia *et al.*, 2011; Nicholson, 1998). This solution had few disadvantages as it had high viscosity and tended to gel with time (low shelf life). This produced a cement with a very high viscosity and low setting rate. Acrylic acid was later co-polymerized with various homopolymer or copolymer of carboxylic acids like acrylic acid, maleic acid, itaconic acid and tricarboxylic acid. The structure of these acids is given in Figure 2.2. These polyacids have different reactivity and strength depending upon the number of carboxylate groups they have (Culbertson, 2001; Lohbauer, 2010). Tartaric acid was added to initial composition of GIC liquid to make GIC more practical system to use. It prolongs the setting time and enhances the working time by delaying formation of the polysalt matrix but at the same time, it also increases the rate of formation of aluminium polyacrylate (Crisp *et al.*, 1979; Culbertson, 2001; Nicholson, 1998; Wilson *et al.*, 1977). Methanol was added to the acrylic acid homopolymer to reduce gelation. This resulted in a reduced number of

intermolecular hydrogen bond formation between the polymer chains resulting in a delayed gelation of the cement (Crisp *et al.*, 1975b).

Water also plays an important role as one of the components of the GIC liquid. It provides the basic reaction medium and is vital for hydration reaction. Water acid ratio is important to maintain as greater quantity of water in the composition leads to a weaker cement (Wilson and Kent, 1972).

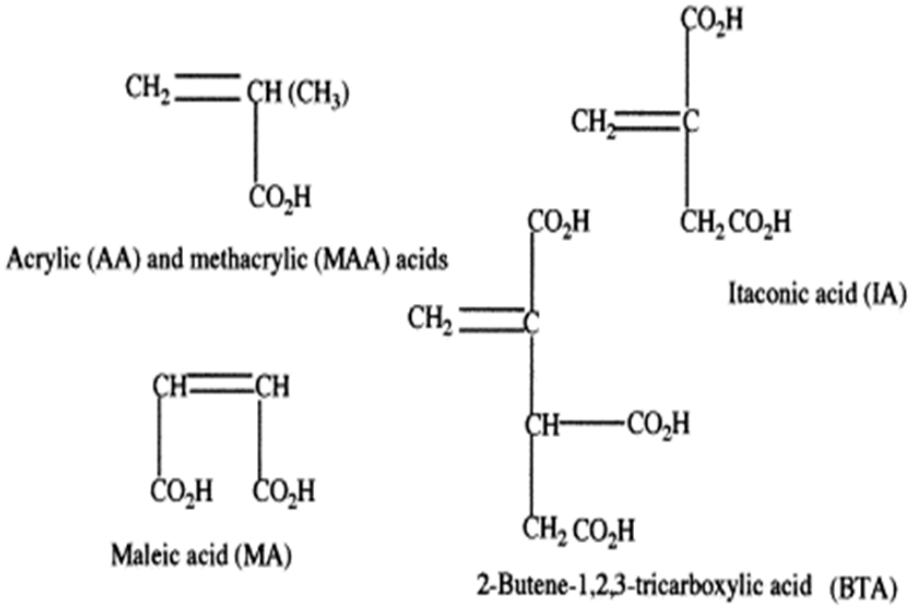

Figure 2.2: Structures of various monomers used for producing glass-ionomer liquid (Culbertson, 2001) (with permission).

2.4 Setting reaction and its mechanism in GIC

Based on their setting reaction glass ionomer cement are known as water-based cement (Crisp *et al.*, 1975a). The mechanism of setting reaction of GIC is complicated and not yet fully

understood. It is primarily an acid-base reaction. When the inorganic glass powder is mixed with aqueous acid solution, a paste or hydrogel is formed as a result of acid-base reaction. Setting or hardening of cement occurs when metal ions from the glass are transferred into the liquid medium resulting in the gelation of the cement (Figure 2.3). This is the most moisture sensitive stage of the reaction as the metal ions are being transferred in a soluble form. Water loss is another reason in the initial setting reaction for solubility, leading to desiccation and disrupting the cement structure. After maturation of cement dehydration is no longer an issue for glass ionomer cement (Craig, 2002; Lohbauer, 2010; McCabe and Walls, 2013; Sidhu, 2015). The setting mechanism of GIC has four phases or stages (Khoroushi and Keshani, 2013).

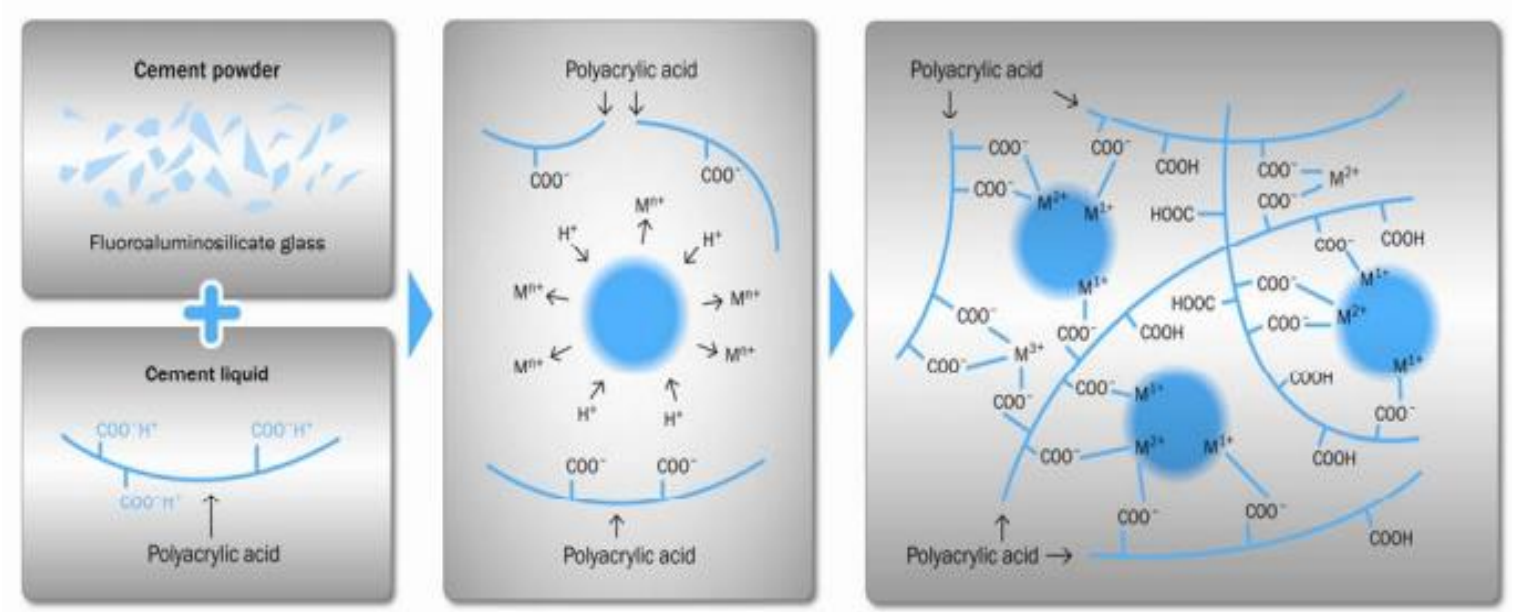

Figure 2.3: Setting reaction of glass-ionomer cement (Lohbauer, 2010) (with permission)

2.4.1 Decomposition of the powder/ion leaching phase

In the first phase of the setting reaction, 20 % – 30 % of inorganic glass particles are attacked by the polyacid. Hydrogen ion produced from the ionization of carboxylic acid reacts with the glass surface that leads to release of metal ions like Ca^{2+}, Al^{3+}, F^{-} and Na^{+} (Figure 2.4) (Cheng *et al.*, 2005). Calcium and aluminium poly-salt bridges will form when Ca^{2+} and Al^{3+} reacts with carboxylic groups of the polyacid and replace the H^{+}. These polysalt bridges will eventually hydrate and create gel matrix (Figure 2.4) (Barry *et al.*, 1979; Cheng *et al.*, 2005; Khoroushi and Keshani, 2013; Lohbauer, 2010).

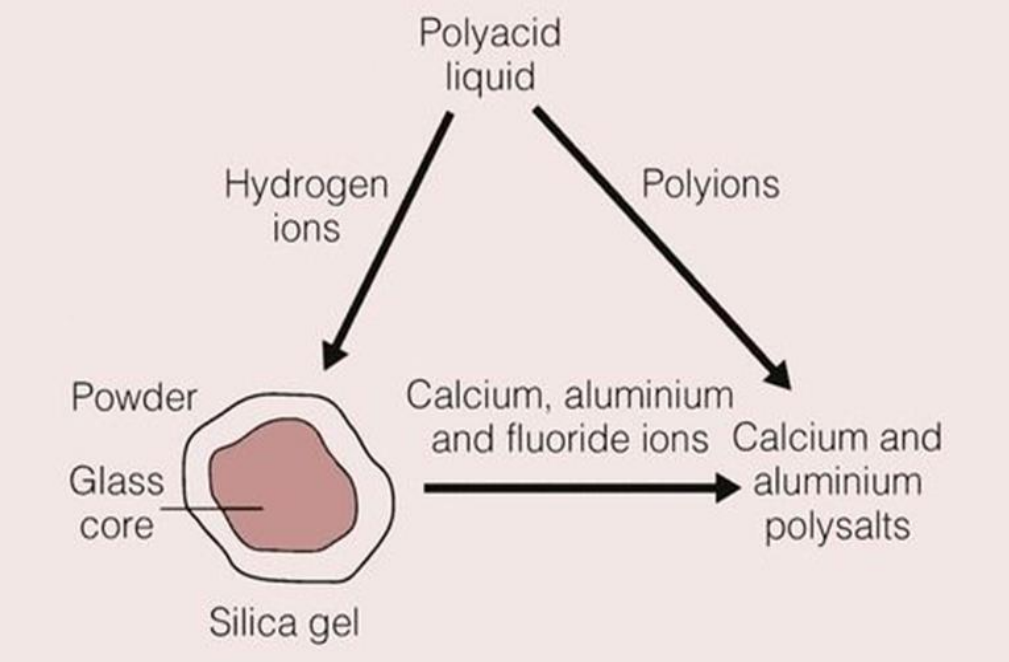

Figure 2.4: Ion leaching phase of GIC setting reaction ("Glass–ionomer and resin-modified glass–ionomer cements," 2018) (with permission).

2.4.2 Gelation phase

This is the second phase of the setting reaction. When the poly-acids attacks and degrades the surface of glass particle leading to metal ion release, Si (Si^{4+}) ions in the form of silicic acid creates a gel around the remaining degraded glass particles. Furthermore, as the concentration of metal ion increases increased number of crosslinking occurs in the GIC matrix (Figure 2.5). As the density of cross-links increases further movement of the metal ions are more and more hindered in their movement towards the carboxyl sites. Therefore, resulting in polyacrylate to gel (Barry *et al.*, 1979; Feng *et al.*, 2015; Khoroushi and Keshani, 2013; Lohbauer, 2010).

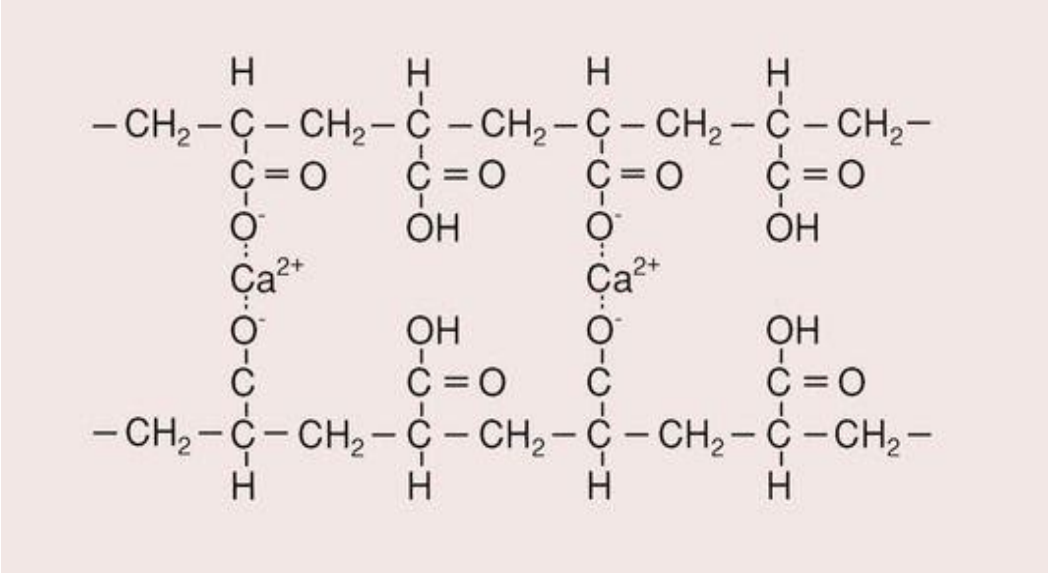

Figure 2.5: Gelation phase of GIC setting reaction ("Glass–ionomer cements and resin-modified glass–ionomer cements," 2018) (with permission).