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EFFECT OF HA ADDITION ON PHYSICAL AND STRUCTURAL OF GIC DERIVED FROM ALUMINO-SILICATE-FLUORIDE BASED GLASS

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By

ZAHIN NAZRIN BIN ROSEMADI

Thesis Submitted to the Department of Physics, Universiti Putra Malaysia, in partial Fulfilment of the Requirements for the Degree of Bachelor of Science in Materials Science with Honours

February 2022

DEDICATION

This dissertation is dedicated to:

- My supervisor, Assoc. Prof. Dr. Khamirul Amin Matori, who has guided and provided advice for me in accomplishing this project.
- My project coordinator, Dr. Shuhazlly Mamat @ Mat Nazir, who has prepared a seminar and workshop related to the preparation of the thesis.
- My family members and my fellow friends who have given the support and help directly and indirectly throughout the thesis writing journey.

ABSTRACT

Effect of HA Addition on Physical and Structural of GIC Derived From Alumino-Silicate-Fluoride Based Glass

By

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February 2022

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Glass ionomer cement is a dental restorative material that is widely used in dental application and usually utilized as a filling and luting material. The conventional GIC is also known for its drawbacks where it is lack in terms of physical, bonding and mechanical properties which limits the usage of GIC in dentistry field as a restorative material. The present work focusses on enhancing the properties of GIC by adding hydroxyapatite (HA) to the GIC. In this research alumino-silicate-fluoride (ASF) glass, polymeric acid (PAA) and deionized water were used to prepare the GIC samples. In order to formulate modified GIC samples, the materials were prepared based on 3:1:1 ratio referring to ASF glass/HA:PAA:H_2O before undergoes ageing process for five different periods of time. All GIC samples were characterized by density measurement, Fourier transform infrared (FTIR), X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM). For certain samples, the inclusion of HA to the GIC samples results in an increase in density measurement. The highest density recorded for the GIC samples was 1.82 g/cm^3 added with 3% of HA at 28 days of ageing time while the lowest density was 1.239 g/cm^3 added with 1% of HA. In addition, XRD, FTIR, and FESEM studies further confirmed the presence of the fluorapatite (FA) crystal phase in the GIC sample. The existence of fluorapatite (FA) crystal peaks was found by XRD analysis of GIC samples, which was confirmed by FTIR research revealed an asymmetric PO stretching mode at a wavenumber of 1020 cm^{-1}. Next, FESEM study of the microstructure reveals the production of spherical particles and agglomerated needle-like structures indicating the formation of apatite crystals. Overall, the addition of HA to GIC improves the physical and structural properties of the material for dental applications.

ABSTRAK

Kesan Penambahan HA terhadap Fizikal dan Struktur GIC Terbitan daripada Kaca Berasaskan Alumino-Silikat-Fluorida

Oleh

Zahin Nazrin Bin Rosemadi

Februari 2022

Pengerusi: Prof. Madya Dr. Khamirul Amin Matori (PhD)

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Simen ionomer kaca adalah bahan pemulihan pergigian yang digunakan secara meluas dalam aplikasi pergigian dan biasanya digunakan sebagai bahan tampalan dan luting. GIC konvensional juga terkenal dengan kelemahannya di mana ia kekurangan dari segi sifat fizikal, ikatan dan mekanikal yang mengehadkan penggunaan GIC dalam bidang pergigian sebagai bahan pemulihan. Kerja-kerja ini memberi tumpuan kepada mempertingkatkan sifat-sifat GIC dengan menambahkan hidroksiapatit (HA) kepada GIC. Dalam penyelidikan ini, kaca alumino-silikat-fluorida (ASF), asid polimer (PAA) dan air ternyahion digunakan untuk menyediakan sampel GIC. Bagi merumuskan sampel GIC yang diubah suai, bahan-bahan telah disediakan berdasarkan nisbah 3:1:1 merujuk kepada kaca ASF/HA:PAA:H_2O sebelum menjalani proses penuaan untuk lima tempoh masa yang berbeza. Semua sampel GIC dicirikan oleh pengukuran ketumpatan, inframerah transformasi Fourier (FTIR), pembelauan sinar-X (XRD), mikroskop elektron pengimbasan pelepasan medan (FESEM). Bagi sampel tertentu, penambahan HA kepada rumusan GIC menghasilkan peningkatan dalam pengukuran ketumpatan. Ketumpatan tertinggi yang direkodkan untuk sampel GIC ialah 1.82 g/cm^3 ditambah dengan 3% HA pada 28 hari masa penuaan manakala ketumpatan terendah ialah 1.239 g/cm^3 ditambah dengan 1% HA. Di samping itu, kajian XRD, FTIR, dan FESEM mengesahkan lagi kehadiran fasa kristal fluorapatit (FA) dalam sampel GIC. Kewujudan puncak kristal fluorapatite (FA) ditemui oleh analisis XRD sampel GIC, yang disahkan oleh penyelidikan FTIR mendedahkan mod regangan PO asimetri pada nombor gelombang 1020 cm^{-1}. Seterusnya, kajian FESEM terhadap struktur mikro mendedahkan penghasilan zarah sfera dan struktur seperti jarum terkumpul yang menunjukkan pembentukan hablur apatit. Secara keseluruhan, penambahan HA kepada GIC meningkatkan sifat fizikal dan struktur bahan untuk aplikasi pergigian.

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APPROVAL

This thesis entitled "Effect of HA Addition on Physical and Structural of GIC Derived From Alumino-Silicate-Fluoride Based Glass" by Zahin Nazrin Bin Rosemadi (Matric No.: 197618), was submitted to the Department of Physics, Faculty of Science, Universiti Putra Malaysia and has been accepted as partial fulfilment of the requirement for the degree of Bachelor of Science in Materials Science with Honours.

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DECLARATION

Declaration by student

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LIST OF ABBREVIATIONS

HA	Hydroxyapatite
GIC	Glass Ionomer Cement
CS	Clam shell
SLS	Soda lime silica
ASF	Alumino-silicate-fluoride
PAA	Polyacrylic acid
FA	Fluorapatite
FHA	Fluorohydroxyapatite
XRD	X-ray diffraction
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
λ	Wavelength
d_{plane}	Distance between the lattice planes
θ	Angle between the incident and lattice plane
ρ	Density
m	Mass
ρ_{sample}	Density of sample
W_{air}	Weight of sample in air
$W_{distilled\ water}$	Weight of sample in distilled water
$\rho_{distilled\ water}$	Density of distilled water
wt.%	Weight percentage
d_{sample}	Average diameter of sample

CHAPTER 1

INTRODUCTION

In this chapter provides a brief overview of the study's history and the effects of adding hydroxyapatite (HA) to glass ionomer cement (GIC). Besides, problem statements and objectives of the study are also stated in this chapter. This is followed by the significance of the study and a thesis outline as a framework, both of which are important to this research.

1.1 Background of Study

Biomaterials play an important role in modern medicine where it is used as restoring function and assisting recovery for patients diagnosed with a disease. Biomaterials can be classified as natural and synthetic biomaterials. Any material derived from plants or animals that is used to augment, replace, or repair biological tissues and organs is referred to as a natural biomaterial (El-Meliegy and Noort, 2012; Parida et al., 2012). While synthetic biomaterial can be grouped as metals, nonbiodegradable polymer, biodegradables polymers and glass and more (El-Meliegy and Noort, 2012). These biomaterials are utilised to support, improve, or repair damaged tissue in the human body.

Glass ionomer cement were first invented by Wilson and Kent 1970 in dentistry field 52 years ago and become one of the most important biomaterials. GIC is a restorative material that is composed of powdered glass and undergoes acid-base reaction with water as a medium for the reaction to occurs. These cements have several excellent properties as a restorative material including thermal compatibility, biocompatibility, and good adhesion to tooth structure. Although GIC have their unique properties as restorative material, it still suffers from few disadvantages such as mechanical properties. Therefore, in order to overcome these weaknesses, there were efforts by previous researchers to improve the properties of GIC. The efforts that have been made were adding fillers into GIC such as hydroxyapatite (HA) and fluoroapatite (FA).

In this project, GIC samples preparation was prepared by using five chemical compounds to produce calcium alumino silicate fluoride glass (ASF). The chemical compounds that were used are soda lime silica glass (SLS), clam shell (CS), calcium fluoride (CaF_2), aluminium oxide (Al_2O_3) and phosphorus pentoxide (P_2O_5). SLS contains high percentage of SiO_2 ranging from (60%-75%), Na_2O about (12-18%) and CaO (5-12%) and as a result, it is a great source of silica for GIC glass preparation. Other than that, CS also is a good source of CaO due to having high percentage of calcium carbonate ($CaCO_3$). CaO can be obtain through calcination process where it converts $CaCO_3$ to CaO for ASF glass formulation.

Adding fillers to GIC samples are one of the methods in improving the properties of GIC. Fillers such as hydroxyapatite, fluorapatite is added to GIC and proven to enhance the hardness and strength as compared to conventional GIC. Hydroxyapatite is known for its beneficial properties such as excellent biocompatibility, similar composition to natural human bone and low solubility in medium. Furthermore, HA has non-toxic, non-immunogenic, non-inflammatory, and bioactive properties, making it an excellent material for therapeutic use, particularly in bone scaffolds and dental implant materials (Rujitanapanich et al., 2014).

1.2 Problem Statement

GIC has gotten a lot of attention and is frequently utilised because of its superior properties to some other traditional dental filling materials. GIC is also popular due to its low toxicity, thermal compatibility, biocompatibility, and other benefits. Other than that, GIC also contain alumino-fluorosilicate glasses which have bioactive properties due to having silicates and fluorides. However, despite having many advantages, GIC still suffers for having few disadvantages such as brittleness, poor wear characteristics, and this has become a major problem and limits their usage in dental industry.

There are several initiatives that had been done by previous researchers in developing new formulations of GIC by enhancing their properties such as incorporation of metal powder into GIC (Irie and Nakai, 1988), addition resin and light curing catalyst (Mitra 1991), resin modified GIC (Souza et al., 2006), incorporated SiC whiskers or short fibres into GIC (Kobayashi et al., 2000) as well as hydroxyapatite fillers (Alatawi et al., 2018). Moheet et al., (2018) predicted that the addition of hydroxyapatite to GIC could improve the mechanical properties. In this research, the addition of HA into GIC is believed to improve the physical and structural properties of GIC.

Next, limited research on different composition of HA used for GIC in order to determine the proper composition of HA added to it. So, different composition of HA was used in this research project to form GIC samples. Due to commercial GIC formulations have poor physical properties, a solution was proposed to improve the physical and structural properties of GIC by varying the ageing time.

1.3 Objectives

Since this research want to analyses GIC using different composition of HA, thus the objectives are:

1. To prepare GIC derive from calcium alumino silicate fluoride glass
2. To investigate the effect of HA added on physical and structural properties of the GIC.
3. To study the impact of setting reaction and ageing time on physical and structural properties of GIC

1.4 Significance of Study

The research of HA added to GIC is important in order to enhance the modified GIC's physical, structural, and mechanical qualities, which are widely used in dental applications. Furthermore, the optimum results of the modified GIC with HA are used to investigate the appropriate ratio of HA to be mixed with ASF glass powder. Since there are limited studies on formulation of GIC with HA, this might lead to more study on formulating ASF glass with HA and how to enhance the physical and structural properties of GIC.

1.5 Overview of Study

Chapter 1 provides a brief introduction of GIC, where it described background of study for GIC. Other than that, it also gives explanations about problem statement, objectives and limitation of study on this project. Next, Chapter 2 provide with a review on related literature reviews which is relevant to this research and background information regarding GIC. Moreover, in Chapter 3 discussed about the preparation and method used in preparing GIC from raw materials. Next, the GIC samples will be characterized into several characterization such as X-ray diffraction (XRD), Fourier Transformation Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM) and density/molar volume. Following that, Chapter 4 will present results and discussion, in which we will examine and evaluate the characterization results. Lastly, Chapter 5 will give overall conclusion for these studies and suggestions for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter will includes literature reports which are relevant with the research and some background information to obtain more knowledge about the conducted research on GIC.

2.2 Development of GIC System

Glass ionomer cement were first introduced to dentistry 52 years ago and have proven to be a valuable addition to restorative dentistry. Adhesion to tooth structure and base metals, anticariogenic properties due to fluoride release, thermal compatibility with tooth enamel, and biocompatibility are just a few of the unique properties that make these cements useful as restorative and adhesive materials (Upadhya and Kishore, 2005). GIC consist of two main component of its composition that are necessary in order to maintain the required properties which are polymeric water-soluble and ion-leachable glass powder (Imran et al., 2019). According to Xie et al. (2000), GIC has low mechanical properties where it is brittle and weak in mechanical properties which limits its clinical use despite having other beneficial properties.

Efforts in improving the mechanical properties of GIC have been made in previous research such as acrylic acid–itaconic acid (AA–IA) copolymers and acrylic acid–maleic acid (AA–MA) copolymers (Crisp et al., 1980), water hardening versions (Mclean et al., 1984), dual-setting resin-modified glass-ionomers (resionomers) (Antonucci et al., 1988) and recent formulation of amino acid residue-modified glass-ionomers (Mitra, 1992). These efforts have been made in order to enhance the mechanical, physical and bonding properties of glass ionomer cement. Some examples of glass ionomer cement incorporated with nanoceramics particles, nanohydroxy and fluoroapatite (Fuji II GC) where the glass ionomer cements containing nano-bioceramics have good restorative dental materials by improving its mechanical properties and improve bond strength to tooth structure (Moshaverinia et al., 2017). These efforts made by previous researchers in order to create an improved material for the future. Material improvement and GIC formulations will improve and further increasing the usage of GIC in dentistry and other medical field.

2.3 Glass Ionomer Cement

GIC can be classified as acid–base reaction cement and is made up of a polyacrylic acid aqueous solution and an acid-decomposable alumino silicate fluoride glass powder (Rayees et al., 2014). The unique characteristics of GIC makes them beneficial for restorative and adhesive materials, such as adhesion to moist tooth structure, anticariogenic properties because of fluoride release, thermal compatibility and biocompatible. Almuhaiza (2016) also mentioned that chemical adhesion to enamel and dentin in the presence of moisture, resistance to microleakage, good marginal integrity, dimensional stability at high humidity, and a coefficient of thermal expansion similar to tooth structure are all advantages of GICs. GIC is a common restorative dental biomaterial for fillings, linings, and adhesion repair (Alatawi et al., 2017). In addition, GIC is also easy to handle and a good biocompatible material in dentistry and other medical application. There are various efforts in developing new formulations of GIC in the course of producing better properties to be applied in the dental and medical industries.

Despite its benefits, GIC has significant drawbacks that prevent it from being widely used in dentistry as a biomedical material. GIC has been shown to have poor mechanical and physical qualities, such as low fracture strength and hardness, decreased wear resistance, and transparency (Rahman et al., 2017). On the other hand, previous researcher also claims that GIC is known for having few disadvantages like brittleness and poor wear characteristics even though it is clinically attractive dental materials (Gu, 2005). Furthermore, GIC is very fragile, indicating that it has insufficient physical strength to be employed as a dental material. The use of GIC as a restorative material is limited because to its high sensitivity to moisture in the early phases of application (Moshaverinia et al., 2011). These weaknesses inspire researchers to do more study in order to enhance the qualities of GIC, particularly in terms of physical and mechanical strength.

2.4 Component of GIC

A glass-ionomer cement requires three ingredients which are polymeric water-soluble acid, basic (ion-leachable) glass, and water (Mclean et al., 1994). One of the major components in GIC are alumino-fluorosilicate glasses which have bioactive properties having silicates and fluorides compound (Najeeb et al., 2016). An acid-base reaction between a polyalkenoic and a simple aluminosilicate glass produces the cement.

2.4.1 Alumino Silicate Fluoride Glass

Fluoride-containing glasses were among the first to be reported when GIC were initially characterized, and they were either of the SiO_2-Al_2O_3-CaF_2 system or the more complicated SiO_2-Al_2O_3-P_2O_5-CaO-CaF_2 system. This bioactive glass or bioglass is more reactive, biodegradable, osteoconductive, and has greater bioactivity than HA (Hench and West, 1996). Bioglass also has a greater bonding ability with both soft and hard tissue and the presence of oxides from silicon, sodium, calcium, and phosphorus in bioglass composition causes them to react with bodily tissues (El-Meliegy and Noort, 2012).

In this study, the composition of ASF glass is consisted of 15 wt.% of CS, 25 wt.% of SLS, 20 wt.% of CaF_2, 20 wt.% of P_2O_5 and 20 wt.% of Al_2O_3. The selection of glass composition is important where each composition responsible in modifying the glass structure and properties in order to meet the glass composition specific needs. The usage of SiO_2 from SLS glass provides glassy network which acts as a network forming and lowering the melting temperature of the glass. The addition of CaO produced from CS functions as a network modifier, modifying the glass structure, reducing the glassy network, and resulting in the creation of crystalline phase inside the samples (Zaid et al., 2020). Meanwhile, the presence of P_2O_5 as a nucleating agent aids the glass system's internal crystallization (Alizadeh and Marghussian, 2000). Next, previous researchers claim that by replacing Na_2O with Al_2O_3 enhance the mechanical properties due to stronger covalent bond in Al–O than Na–O. Calcium fluoride (CaF_2), which is made up of calcium ions (Ca^{2+}) and fluoride ions, has an effect on the characteristics of the glass system (F^-). In fact, the fluoride ion is frequently used in glass characterization because it has the potential to modify the nature of glass material for dental purposes.

2.4.2 Polymeric acid

Polyacrylic acid, polyitaconic acid, polymaleic acid, or a copolymer of these acids are the most common polyalkenoic acids that have been used in producing GIC. Previous research has been made stating that polyvinyl phosponic has been used in preparing GIC and proven to be as a potential cement former (Ellis and Wilson, 1990). McCabe et al. (2008) states that polymeric acid added to formulations of GIC will enhance the working time and the cement's setting reaction, allowing for easier and better cement manipulation. The properties of the glass-ionomer cement made from them are influenced by the polymer. Sidhu and his co-workers claim that high molecular weight of polymeric acid will increase the setting strength of the cement, but making it difficult to mix due to having high viscosities (Sidhu et al., 2016). Hence, appropriate amount of polymeric acid used in GIC has to be taken into consideration.

2.4.3 Role of water

Next, the type of solvent used for GIC is water where it is the third important component of GIC and to initiate the acid-base reaction. Furthermore, water also play several important roles such as allowing polymer to act as an acid through proton release and one of the components for setting reaction for GIC to occurs (Sidhu et al., 2016). This statement is proven by one of the researcher's findings where it serves as a solvent for the polymeric acid and helps the polymer to behave as an acid by facilitating proton release. It is also act as a medium where the setting reaction takes place (Nicholson, 1998). According to Caluwe et al., (2017) the presence of water or a tartaric acid aqueous solution is needed for the formation of a GIC. However, adding too much of water to GIC will cause metal cation to dissolute and disturbs the setting reaction of GIC (Lohbauer, 2010).

2.5 Classification of GIC

GIC can be classified into three types which is Type I, Type II and Type III. The usage of these type of GIC are depends on how they are applied and clinically used in the dentistry field (Wilson and Kent, 1972). Type I GIC usually used for crowns, bridges, inlays, onlays and orthodontic appliances and was made for luting and bonding of cements. This type of GIC uses low powder to liquid ratio which gives them moderate in terms of strength. Next, Type II GIC is a restorative cement and can be divide into two category which is Type II (i) is used for anterior repair and have aesthetic values. On the other hand, Type II (ii) is used for posterior restoration and repairs where appearance is not taken into account. Similarities of these category is that they use high powder to liquid ration and are usually radio opaque. Lastly, Type III is for lining or base cements and are use in preventing dental caries and made from low powder to liquid ratio for good adjustment to the cavity walls. Sidhu and Nicholson (2016) stated that the type of GIC uses the same composition but different in powder to liquid ratio depending on their application and uses in dentistry field.

Table 2.1: Classification and classes of GIC (Sidhu et al., 2016)

Type I:	Luting and bonding cements.
Type II:	Restorative cements • Type II (i): Anterior repair involving aesthetics properties • Type II (ii): Posterior repair where aesthetics properties is not involved
Type III:	Lining or base cements

2.6 Mechanical properties of commercial GIC

GIC still have their weaknesses despite having excellent properties including brittleness, low mechanical properties, long term setting time, rough surface texture, low fracture toughness, and low wear resistance which restricts their clinical use. These restorative materials' low wear resistance is due to their lack of strength shortly after application and susceptibility to acids (Poorzandpoush et al., 2017). There are few studies reported that the commercial GIC recorded a lower value in compressive strength compared to modified GIC. For example, researchers from Germany reported that conventional GIC had compressive strength of 78.8 MPa, while modified GIC had 169.50 MPa (Daniela et al., 2015). In the same research studies also studied that conventional GIC had low wear resistance than modified GIC. This statement can be proven where it is recorded that conventional GIC had the largest damaged area in wear test and the damaged area is 2.403 mm^2 (Daniela et al., 2015). On the other hand, the modified GIC had lower damaged area 1.793 mm^2. These compressive strength and wear test demonstrates that modified GIC is better than conventional GIC in terms of mechanical properties.

2.7 Hydroxyapatite

The drawbacks from conventional GIC expands the extensive research on improving the physical and structural properties as well as the mechanical properties of GIC. There have been numerous approaches used in previous studies to improve the properties of GIC.. Incorporating HA into GIC as fillers is one of the methods that can been done to improve the conventional GIC in terms of its properties.

2.7.1 Definition, properties and application of HA

Hydroxyapatite (HA) is a calcium phosphate bioceramic with a calcium to phosphorus ratio of 1.67 with molecular formula of $Ca_{10}(PO_4)_6(OH)_2$ (Goenka et al., 2012). Hydroxyapatite (HA) is a biocompatible material with a composition and crystal structure identical to apatite that is found in the human dental and skeletal systems. The composition of hydroxyapatite is similar to that of dental hard tissues. As a result, they've been used as a filler in restorative materials quite often. Hydroxyapatite has the ability to integrate with bone structures that will help in bone bonding and support bone ingrowth without breaking down or dissolving the implant. In addition, HA contain inorganic matrix of human bone in a form of phos-phocalcic hydroxyapatite and contains phosphate and hydro-xyl ions (Moshavarienia et al., 2008). Furthermore, HA also has additional benefits, such as being non-toxic, non-immunogenic, non-inflammatory, and bioactive, making it a suitable material for clinical use, particularly in bone scaffolds and dental implant materials (Fathi et al., 2008).

In recent years, hydroxyapatite (HA) has proven promising properties in restorative dentistry, including biocompatibility, and hardness similar to natural bone. In fact, HA has been used as a reinforcement material in adhesive bone cements and dental composites Arita et al., (2003). Rayees et al. (2014) also stated that due to having excellent bioactive properties and favourable osteo-conductive, HA has played an important role in orthopedics applications. As shown in Figure 2.1 (Szcześ et al., 2017), HA is commonly used in bone scaffolds and bone fillers, implant coatings, and drug delivery systems. The application of HA in dentistry is encouraged by the nature of tooth enamel, which contains a majority of inorganic calcium phosphate of HA. HA has been employed as fillers in restorative GIC as well as composite resin, pulpotomy and direct pulp capping agent, fillers in endodontic root canal sealers, and treatment of early carious lesions. (Kantharia et al., 2014).

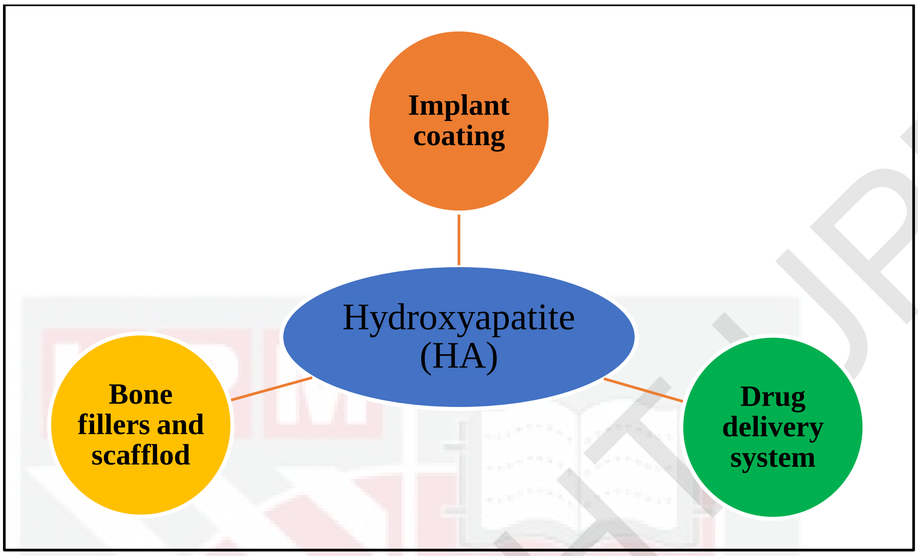


Figure 2.1: HA application in biomedical industry (Szcześ et al., 2017)

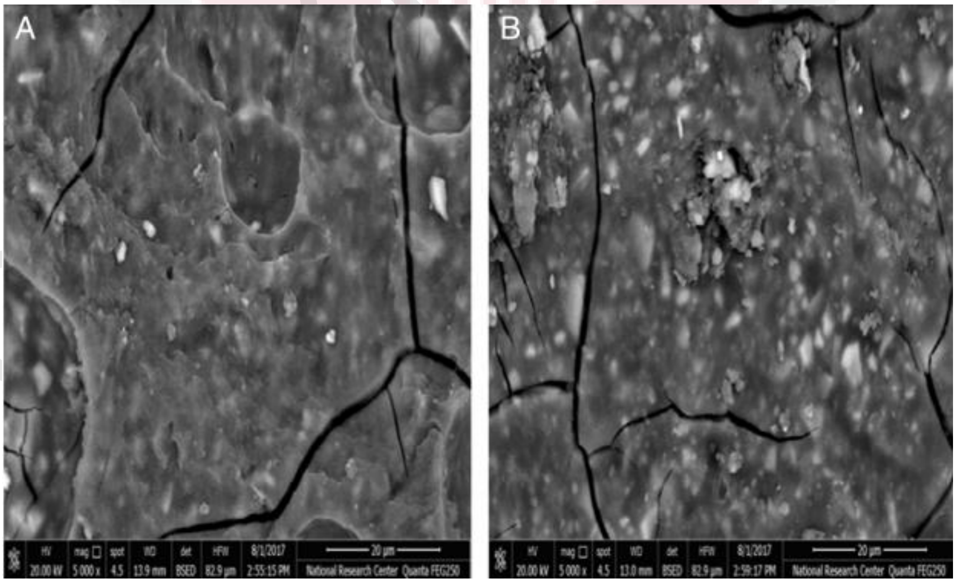
2.7.2 Effects of HA addition to GIC

Barandehfard (2016) reported that GICs have been identified to interact with HA via the polyacid's carboxylate groups. As a result, adding HA to GICs system could improve their biocompatibility as well as their mechanical properties. There were significant efforts that has been made in improving and overcome the problems by using fillers added to the GIC cement such as hydroxyapatite (Gu et al., 2005). Previous research studied that addition of HA to the GIC samples will increase its crystallinity and improves mechanical properties and creates a positive environment for enamel remineralization (Moheet et al., 2018). Another research findings by Barandehfard et al. (2016) stated that due to the crystalline growth caused by the presence of nanoceramics, the compressive strength of the glass ionomer containing nanoceramics was increased. As a result, samples containing FA had a greater compressive strength than samples including HA due to their higher degree of crystallinity in contrast to nano HA. Moheet et al., (2018) also found that glass ionomer cement that was added with nano-hydroxide silica improves hardness, compressive strength, and flextural strength in comparison to conventional GIC. Lucas et al. (2003) studied that adding HA particles to the glass ionomer powder increased the cement's fracturing toughness, allowing it to maintain a long-term bond to the dentin. Moshaverienia et al. (2008) also studied that addition of nanohydroxyapatite/fluoroapatite as fillers to GIC obtain higher compressive strength and higher bond strength to tooth structure.

2.8 Physical and structural properties of GIC

GIC has several disadvantages in terms of physical properties such as brittleness, poor colour range and lacks of translucency. There are several efforts that have been made in order to improve these drawbacks and nowadays the colour range and translucency is much better (Mount, 1988). Other than that, Najeeb et al. (2016) stated that the surface roughness and hardness is lower than the modified GIC no matter what size of fillers incorporated into them. A study has been made by group of researchers where it is found that the surface roughness between fillers incorporated with GIC and the conventional GIC are showing relatively large value changes (Daniela et al., 2015). The modified GIC recorded roughness value below 0.2 µm which is lower than the conventional GIC. The high surface roughness will affect the aesthetic values as well as the mechanical properties of a GIC. Therefore, researchers nowadays have improvised the conventional GIC by adding fillers such as nanofillers to lower the roughness values and consequently polishing.

Previous studies from researchers have found an extensive finding where the structural properties were obtained from characterization of GIC. Moshaverinia et al. (2008) discovered that the XRD findings revealed that the produced bioceramics exhibited low levels of impurity, high levels of crystallinity, and structures that were linked to the chemical compositions of hydroxyl and fluorapatite (FA). As a result of the addition of fluorine to the HA matrix, the crystallinity of the final crystals rose. The enhanced crystallinity of the FA bioceramic nanopowders corresponded to an improvement in chemical stability. Another research studies found that the nano-sized HA and HA/ZrO_2 have needle-shape structure which are from HA while ZrO_2 have spherical powder using SEM analysis (Gu et al., 2005). From studies that have been made by Alatawi et al. (2018), SEM analysis was used to investigate the structure of conventional GIC and GIC incorporated with 8% of HA. Figure 2.2 demonstrates that the attack of freeze-dried acidic polymers on the basic glass powder causes matrix surface breaking and degradation, resulting in the release of metal and non-metal ions.



C-GIC GIC-HA hybrid

Figure 2.2: SEM of C-GIC and GIC-HA hybrid (Alatawi et al., 2018)

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter will discuss about methods and procedures used in preparing GIC samples by using glass frits from ASF glass with addition of commercial HA, deionized water and PAA. In this chapter also discusses the effect of different HA composition on GIC in order to determine the optimal amount of HA added to the samples. Apart from that, density measurement, XRD, FTIR and FESEM were used to analyze the physical and microstructure of the GIC. Figure 3.1 shows the process of preparing the GIC samples.

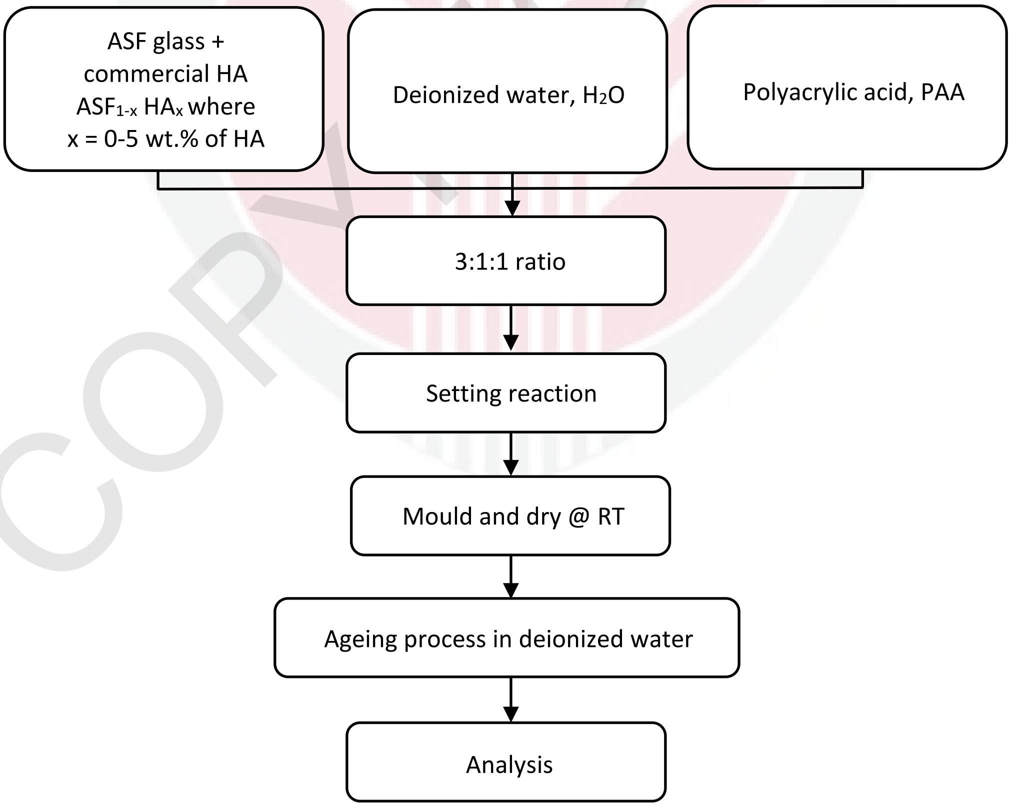


Figure 3.1: Process of preparing GIC samples

3.2 Sample preparation

Preparation of GIC samples were started with the preparation of the raw materials which are alumino-silicate-fluoride glass powder, polyacrylic acid, PAA and deionized water, H_2O. These are the main part of preparing GIC samples by following a 3:1:1 ratio with deionized water and PAA followed by adding HA to ASF glass. The preparation of GIC samples with formulation of ASF glass and different composition of commercial HA are also explained in this section.

3.3 Preparation of raw materials

Preparation of raw materials was done by preparing glass frits of ASF glass before mixing it with HA and PAA. ASF glass powder was first characterized from CS powder, SLS powder, CaF_2 powder, P_2O_5 powder and Al_2O_3 with composition represented by formula $15CS \cdot 25SLS \cdot 20CaF_2 \cdot 20P_2O_5 \cdot 20Al_2O_3$. This mixture was milled and underwent a melting process at 1500° C for 4 hours using electrical furnace as shown in Figure 3.2. The molten glass was rapidly cooled in water to produce glass frits. The glass frits that were obtained in the quenching process were left to dry at room temperature before being crushed on the next day by using a plunger (Figure 3.3). The plunged glass frits were grinded using mortar and pestle in Figure 3.4. By using 45 μm siever in Figure 3.5, the glass was sieved in order to get a fine ASF glass powder.

Figure 3.2: Electrical furnace for melting process

Figure 3.3: Plunging apparatus used for crushing ASF glass frits

Figure 3.4: Mortar and pestle

Figure 3.5: 45 µm powder siever

3.4 Formulation of ASF with commercial HA

Production of ASF glass and HA composites were produced by using different composition of HA which is 0-5 wt.%. ASF glass were mixed with a different composition of commercial HA and were weighed by using analytical balance according to Table 3.1. Then the mixed powder was milled for about 15 minutes until homogenous mixture of ASF glass and HA composite powder was achieved. Steps of formulating ASF glass with HA were repeated from preparing raw materials with different ratio of commercial HA composite powder as shown in Table 3.2.

Table 3.1: Formulation of ASF glass and HA

Type of GIC	ASF (grams)	HA (grams)	Total (grams)
$ASF_{1.00}HA_0$	9.00	0.00	9
$ASF_{0.99}HA_{0.10}$	8.91	0.09	9
$ASF_{0.98}HA_{0.20}$	8.82	0.18	9
$ASF_{0.97}HA_{0.30}$	8.73	0.27	9
$ASF_{0.96}HA_{0.40}$	8.64	0.36	9
$ASF_{0.95}HA_{0.50}$	8.55	0.45	9

3.5 Preparation of GIC samples

Preparation of GIC samples includes three important materials which are ASF glass with HA powder, PAA and deionized water. In order to fabricate a GIC sample, an acid-base reaction technique was carried out where the ASF glass powder is alkaline and PAA is an acidic solution. Polymer, PAA with molecular weight of 30,000 were used in the fabrication of GIC samples. These materials were mixed together with a ratio of 3:1:1 of $ASF_{1-x}HA_x$: PAA: H_2O where x = 0.0-0.5 wt.% of HA. The mixture was generously mixed by using a spatula for about 60 seconds until homogeneous mixture was achieved. This stage is where the setting reaction of the cement occurs.

Table 3.2: Ratio of Glass:PAA:H_2O for preparation of GIC

$ASF_{1-x}HA_x$	PAA	H_2O	Ratio $ASF_{1-x}HA_x$:PAA:H_2O
3	1	1	3:1:1

3.5.1 Moulding and Pelleting

The mixture of the GIC samples were placed into a specific stainless-steel mould where the size was 6 mm in height and 4 mm in diameter. Then, the GIC samples inside the mould undergoes a pellet process where the moulds were pressed between stainless steel plates as shown in Figure 3.6. Then, the pellets were pressed by using a hydraulic pressure machine and the applied force is about 5 tons. The moulds were transferred and put in the electric oven at 37 °C for 1 hour.

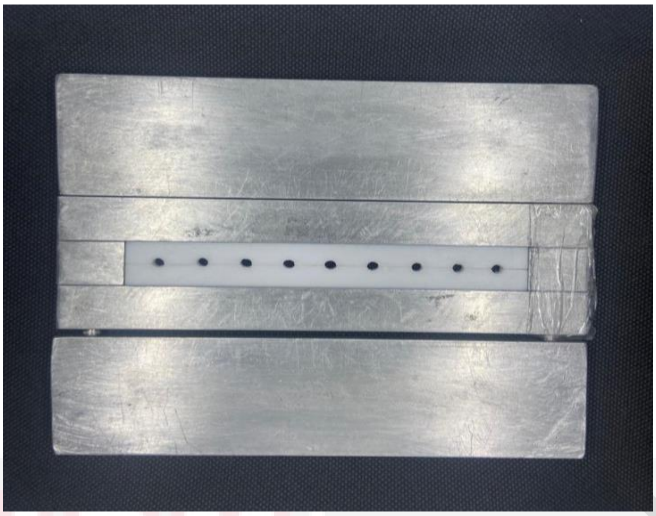


Figure 3.6: Moulding tool used in fabricating the GIC samples

3.5.2 Ageing Time

After the drying process, the GIC samples were then undergoes ageing process for about 1, 7, 14, 21 and 28 days in 10 ml of deionized water which act as a medium for the reaction to occur after the samples were taken out from the mould. The samples were placed in the water to enhance the mechanical properties of GIC samples. This process will take almost 28 days in order for the samples to harden.

3.6 Characterization of GIC

The samples of GIC were characterized to determine the physical properties and the microstructure before GIC preparation. The samples were characterized by using several pieces of equipment. The measurements that were used are XRD, FTIR, FESEM and density measurement.

3.6.1 Density measurement

Density can be defined as the tightness of a particle packed inside the material. The higher the density of a material, the closer the particles are packed together. Density can also be defined by equation below:

$$\text{Density} = \frac{mass}{volume}$$

The Archimedes concept was used to determine density at room temperature. According to the Archimedes principle, the apparent weight of a submerged item will be less than the real weight by the quantity of fluid displaced. Using an electronic balance with a $\pm$ 0.001 g precision, the sample was weighed in air and water, W_{air} and W_{water}, respectively. Water has a density of 1.00g/cm^3, so the density of a sample can be express as:

$$\rho_{sample} = \frac{W_{air}}{W_{air} - W_{water}} \times \rho_{water}$$

Where,

ρ_{sample} = density of sample

W_{air} = weight of sample in the air

W_{water} = weight of sample in the water

ρ_{water} = density of distilled water

3.6.2 Fourier Transform Infrared Spectroscopy (FTIR)

Transform of the Fourier Series Infrared Spectroscopy, commonly known as FTIR Analysis or FTIR Spectroscopy, is a method for identifying organic, polymeric, and inorganic materials. Infrared light is used to scan test materials and examine chemical characteristics using the FTIR analysis technique. FTIR analysis measures a broad range of wavelengths in the infrared region that are absorbed by the samples. This can be achieved when the infrared radiation is directed to the samples of a material. Molecular composition and structure of a material can be determined when the samples absorb infrared light's energy at various wavelengths. Absorbed infrared radiation excites molecules into a higher vibrational state when a material is irradiated with it. The energy difference between the at-rest and excited vibrational states determines the wavelength of light absorbed by a specific molecule. The wavelengths that the sample absorbs are indicative of its molecular structure. Characteristics of the molecular structure are determined by wavelengths that are being absorbed by the samples. In this project, FTIR characterization was carried out to determine the chemical bonding of the GIC samples. The UTAR-FTIR (Universal Attenuated Total Internal Reflection Fourier Transform Infrared) spectra obtained using a Thermo Scientific Nicolet 6700 FT-IR spectrometer in the range of 4000-400 cm^{-1} with a resolution of $4cm^{-1}$ were used to evaluate the samples.

3.6.3 X-ray diffraction (XRD)

XRD is usually used to identify unknown crystalline materials and obtain information about the microstructure of materials. A cathode ray tube produces the X-rays, which are then filtered to create monochromatic radiation, collimated to focus the beam, and directed onto the sample. The interaction of the incident ray to the samples creates constructive and destructive interference where this process is called diffraction. The diffraction of X-rays by crystals is only when the conditions satisfy Bragg's Law. The application of Bragg’s law in XRD spectroscopy was shown in Figure 3.7. The wavelength of electromagnetic radiation is related to the diffraction angle and lattice spacing in a crystalline sample by this law. The Bragg’s Law can be described as:

$$n\lambda = 2d \sin \theta$$

Where,

λ = wavelength of x-ray

d = spacing of the crystal layers

θ = incident angle

n = integer

The two theta positions which correspond to a certain spacing between the crystals or atoms in the sample are determined by the angle of diffraction from the incoming x-ray beam transmitted into the sample. The number of molecules in that phase or the distance between them determines the strength of the peaks. The more intense the peak, the more crystals or molecules present with that exact spacing.

The sample powder was sieved to a size of 45 m in this research before being examined using XRD. The machine used is a PW 1830 model from PANalytical (Philips, PW3040/60). At 40 kV and 30 mA input current, Cu K_α radiation, $\lambda = 1.5418$ was applied. Within Bragg's angle, the XRD pattern was observed in a range of 20° to 80°. The findings were analysed using PANalytical X'pert Highscore software, and the sample phase was classified using the International Center Diffraction Data (ICDD) database.

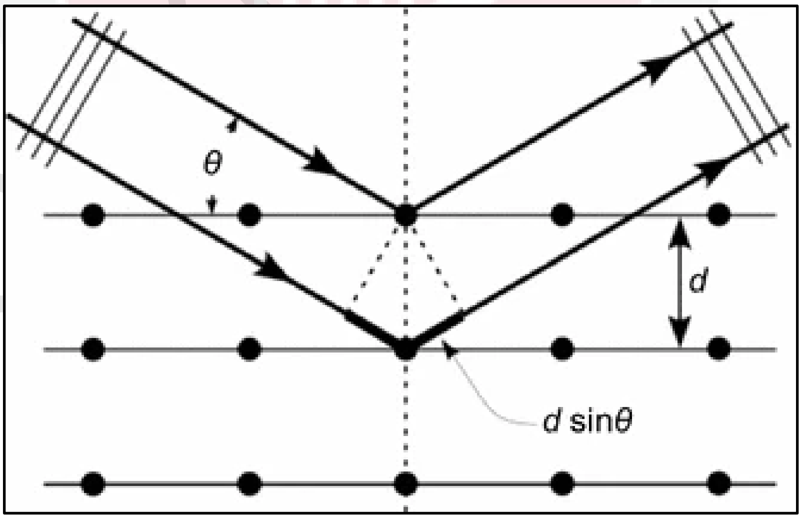


Figure 3.7: Schematic representation of the Bragg's equation (Mandal, 2008)

3.6.4 Field Emission Scanning Electron Microscopy (FESEM)

The field emission scanning electron microscope (FESEM) is a type of electron microscope that uses a high-energy beam of electrons to scan the sample surface in a raster scan pattern to image it. At magnifications ranging from 10× to 300,000×, FESEM delivers topographical and elemental information with nearly infinite depth of field. FESEM collects a wide range of information from the sample surface, but at a better resolution and with a much larger energy range. It also produces high-resolution, low-voltage images with minimal sample electrical charge. The FESEM was carried out with the FEI Nova NanoSem 230 high resolution field emission Sem, which is the primary imaging instrument for nanoparticles, with a resolution of 1 nm at 15 kV. In this research, the sample was attached to the sample holder in powder form, sieved at 45 µm size, before being coated with silver to avoid charging which might create blur in the image produced. The sample was then placed into an FEI NOVA NanoSEM 230 FESEM machine with a magnification of up to 200 000×.

CHAPTER 4

ANALYSIS AND DISCUSSION

The results and analysis obtained in sample characterization will be discussed and presented thoroughly in this chapter. The samples were characterized using different types of analysis which is density measurement, XRD, FTIR, and FESEM.

4.1 Density measurement of GIC samples with addition of HA for different composition of HA and ageing time

In this part, the density results and molar of GIC samples with the addition of hydroxyapatite were shown and discussed. The Archimedes method were used in order to determine the densities of the GIC samples.

Table 4.1: Density of GIC sample at different HA composition and different ageing time

Different ageing time	Density at different composition of HA					
	0%	**1%**	**2%**	**3%**	**4%**	**5%**
1 day	1.773	1.239	1.641	1.708	1.718	1.624
7 days	1.757	1.680	1.754	1.736	1.719	1.407
14 days	1.698	1.734	1.736	1.734	1.760	1.765
21 days	1.799	1.798	1.810	1.827	1.704	1.779
28 days	1.693	1.676	1.790	1.820	1.792	1.785

Table 4.1 presents the density results of GIC samples with different concentration of HA which undergoes different ageing time process. Figure 4.1 shows the overall trend for the of GIC samples incorporated with different composition of HA in different ageing time. Based on the density results obtained in density measurement, it is observed that the density results of GIC samples increases with ageing time from 1 to 21 days except for 0% of HA which shows a decrement in density value. According to previous researcher, the change in the ratio of bound to unbound water causes the GIC samples to become denser as the ageing time increases (Khiri et al., 2020). Furthermore, HA concentrations ranging from 1% to 4% increased the density value of GIC samples. On the other hand, GIC samples containing 5% HA showed a significant reduction in density value for 14 and 21 days of ageing time. This is due to the HA particles operate as a barrier and limit complete bonding in the GIC matrix, resulting in a drop in density value (Nicholson et al., 1993).

The highest density recorded for the GIC samples was 1.82 g/cm^3 added with 3% of HA at 28 days of ageing time. Meanwhile, the lowest value of density recorded for the GIC samples was 1.239 g/cm^3 added with 1% of HA soaked in deionized water for 1 day. High value of density is due to the growth on the surface of the samples of FA crystals. This claim may be supported by an XRD analysis that demonstrates the growth of FA crystal in the GIC structure against the ageing time.

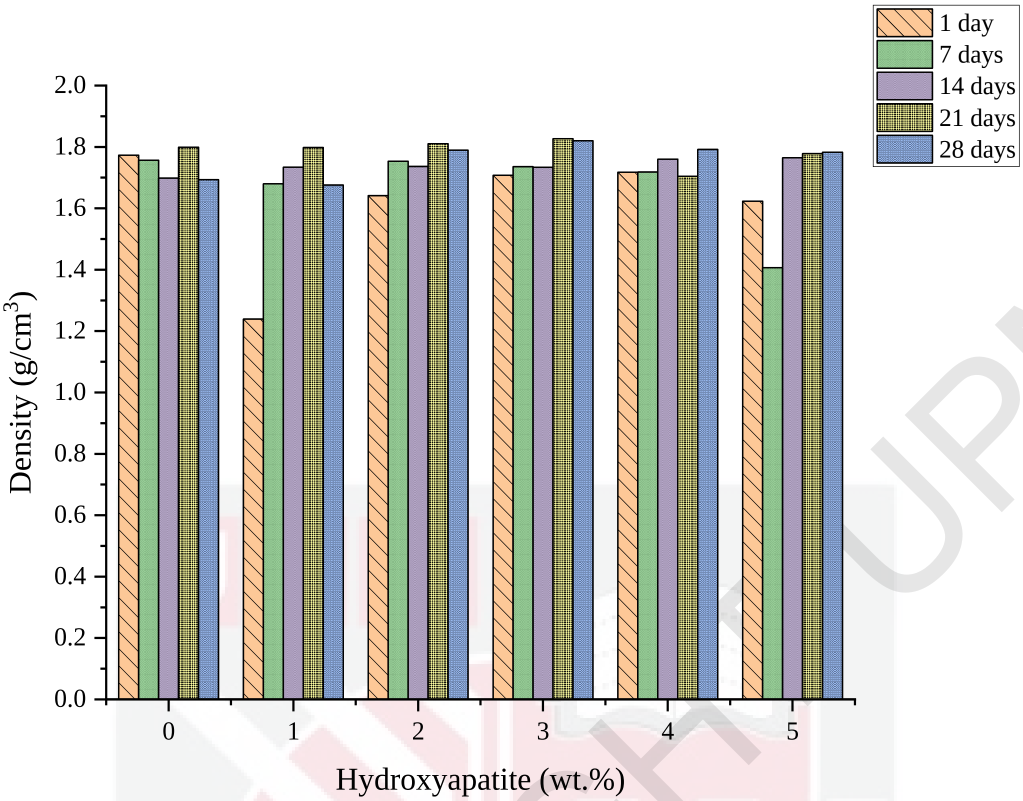


Figure 4.1: Density of GIC with different composition of HA and different ageing time

e4.2 Fourier Transform Infrared Spectroscopy (FTIR)

In this section, the FTIR results of GIC samples with 0% composition of HA that were subjected to 7, 14, 21, and 28 days are presented and analysed. This section also discusses and explains the chemical bonds identified in the control GIC samples. Figure 4.2 showed the FTIR pattern for GIC samples at 7, 14, and 28 days of ageing time, whereas Table 4.3 showed FTIR spectral bands corresponding to the vibrational modes found in the cement samples. It is found that several peaks emerged at wavenumbers of ~440, ~570, ~600, ~1020, ~1460, ~1550 cm^{-1}, and a wide peak at ~3400 cm^{-1}. According to the FTIR analysis, there is no much difference between the GIC samples even though various ageing time is subjected to the samples.

The development of a spectral band at 440 cm^{-1} was due to the double degenerate O–P–O bending mode which indicated as the phosphate group in the apatite sample, or the Si–O–Si vibration mode from the usage of SLS glass in producing GIC samples. Then there was the appearance of a triple degenerate O–P–O bending mode at both peaks at wavenumbers ~570 and ~600 cm^{-1}. At a strong peak of ~1020 cm^{-1}, another phosphate chemical bonding was detected which indicated the asymmetric P–O stretching mode. The existence of a carbonate precursor in the production of GIC samples was demonstrated by the carbonate group exhibited by the CO vibration mode at wavenumber ~1460 cm^{-1}. The formation of an asymmetric COOH band at ~1500 cm^{-1} is due to the carboxyl group from PAA used in the formulation of GIC. Then, at a high frequency of ~3400 cm^{-1}, a large absorption band was detected, indicating the presence of an OH vibration mode.

Table 4.2: The vibrational modes of the control GIC sample assigned to an FTIR spectral band (Wan Jusoh et al., 2021).

Wavenumber (cm^{-1})	**Assignment of vibrational mode**	**Reference**
~440	O–P–O bending mode	Mandal et al. (2014), Zarifah et al. (2016),
~570, ~600	O–P–O bending mode	Moshaverinia et al. (2008), Goenka et al. (2012), Garcia-Contreraset al. (2015), Barandehard et al. (2016), Alatawi et al. (2019)
~1020	asymmetric P–O stretching mode	Mandal et al. (2014), Zarifah et al. (2016)
~1460	C–O vibration mode	Moshaverinia et al. (2008)
~1550	Asymmetric COOH mode	Khiri et al. (2020)
~3400	OH vibration mode	Montazeri et al. (2011), Jekonovic et al. (2013)

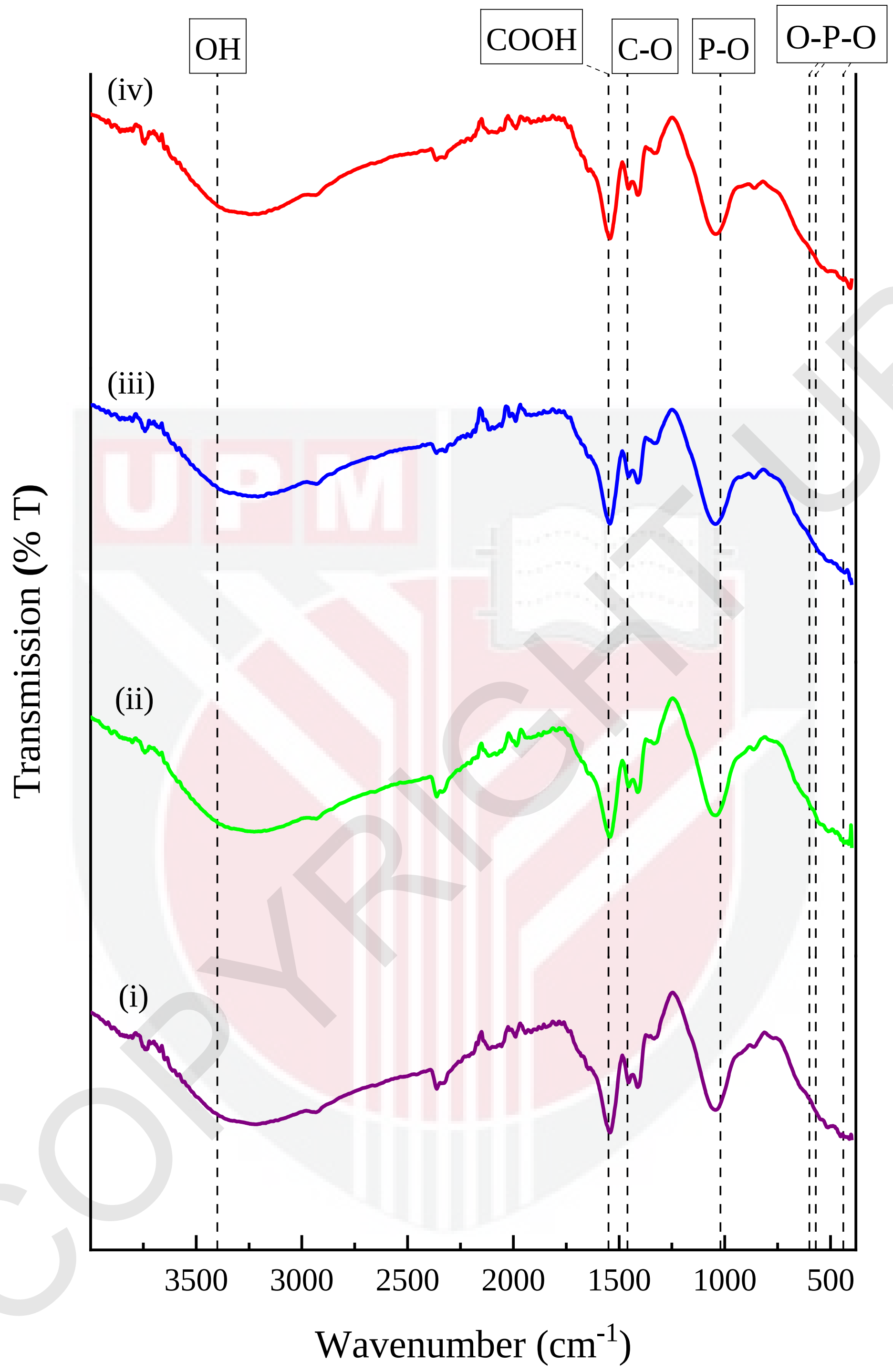


Figure 4.2: FTIR pattern for GIC samples with 0% of HA at (i) 7 days, (ii) 14days, (iii) 21 days and (iv) 28 days of ageing time

4.3 X-ray Diffraction (XRD)

The XRD results that were obtained in the analysis procedure for the GIC samples with different amount of HA and ageing time were presented in the graph below. According to the Figures 4.3 until 4.8, fluoroapatite (FA) crystal peaks were observed in all GIC samples. From the XRD pattern, it can be observed that no much difference can be seen between the samples even though different amount of HA added to the samples with various ageing time process. However, the intensity of peak was seen to be higher at 21 days of ageing time in all modified GIC samples. The highest intensity of crystal peak was observed at about 2θ = 31.9° in the range of 1224.2 to 2057.2 a.u. for the samples.

Figure 4.3 shows the XRD pattern of GIC samples without the addition of HA aged in deionized water for 1-28 days. Based on the figure below, it is shown that the highest crystal peak was detected at about 32° with the intensity values of 2057, 1860, 1619, 1711, 1641 a.u. The XRD pattern of the GIC samples showed the almost the same pattern even though different ageing time were proposed. From the XRD analysis, the pattern of the highest intensity peaks decreasing from 1 day to 14 days and rise at 21 days of ageing time. The highest intensity peaks recorded for this sample is at 2057 a.u at 1 day of ageing time while the lowest value of highest intensity peaks is at 1619 a.u at 14 days of ageing time.

Meanwhile, Figure 4.4 illustrates the XRD pattern of GIC samples added with 1% of HA subjected to different ageing time from 1 day until 28 days. The highest intensity peak was detected in the GIC samples at about 31.9° with intensities of 1542, 1447, 1657, 1772 and 1516 a.u for 1, 7, 14, 21 and 28 days of ageing time. From the XRD analysis, it can be seen that the pattern of the highest peaks for different ageing days is increasing from 7 days to 21 days and the value of intensity dropped at 28 days. The highest intensity peaks of crystal peaks recorded for 1% HA samples is at 21 days 1772 a.u.

Next, Figure 4.5 indicates that the XRD pattern of GIC samples added with 2% of HA subjected to different ageing time from 1 day until 28 days. From the figure below, it can be seen that the pattern of the XRD is almost the same compared to 1% of HA. On the contrary, the intensity of the crystal peaks is much higher compared in 2% compared to 1% of HA. Based on the XRD analysis, the crystal phase formed is FA. The highest intensity of crystal peaks are increasing from 1 day to 7 days with the intensity of 1638 and 1701 a.u respectively and then dropped at 14 days of ageing time with intensity of 1631 a.u. The crystal peaks were then increase from 14 days until 28 days with intensity of 1631, 1696 and 1791 a.u.

On the other hand, pattern in Figure 4.6 shows XRD pattern of GIC with 3% HA demonstrated the development of FA crystal phase even at the early stage of ageing time. Except for the strength of the crystal peak, no progressive change in the crystal peak was detected from GIC samples of various ageing times. Based on the crystal peaks shows in Figure 4.6, the intensity of the peaks was seen to be increasing from 1 days to 14 days of ageing time with 1224, 1273 and 1737 a.u respectively. The intensity of crystal peaks decreases at 21 days of ageing time with the value of 1687.866 and increase at 28 days with 1714 a.u.

Based on XRD pattern shown in Figure 4.7, it is shown that the GIC samples with 4% of HA have the highest intensity of crystal peaks compared to other samples. The highest peaks recorded for this sample was at 21 days of ageing time with the value of 1827 a.u at $2\theta = 32°$. Compared to the other samples, GIC that contains 4% of HA have the highest intensity of peaks due to having high crystallinity which results higher crystal peaks. The existence of FA's crystal peak is due to the CFAS glass-ceramics unstable chemical composition (Rahman et al., 2019). Furthermore, the effect of CaO in the chemical composition of CS as a network modifier that enhanced the crystallization of the CFAS glass.

Figure 4.8 shows the XRD pattern for GIC samples that contain 5% concentration of HA subjected to 5 different ageing time which are 1, 7, 14, 21, and 28 days. Based on the XRD pattern analysis it is found that the crystal peaks decrease as the ageing time increase. The highest crystal peaks for this sample decreases from 1 day to 14 days of ageing time. The highest intensity peaks were then slightly increase at 21 days before decrease again at 28 days. The highest crystal peaks recorded were 1604, 1529, 1503, 1549 and 1507 a.u for 1, 7, 14, 21 and 28 days. The highest crystal peaks formed at about the same diffraction angle for all samples

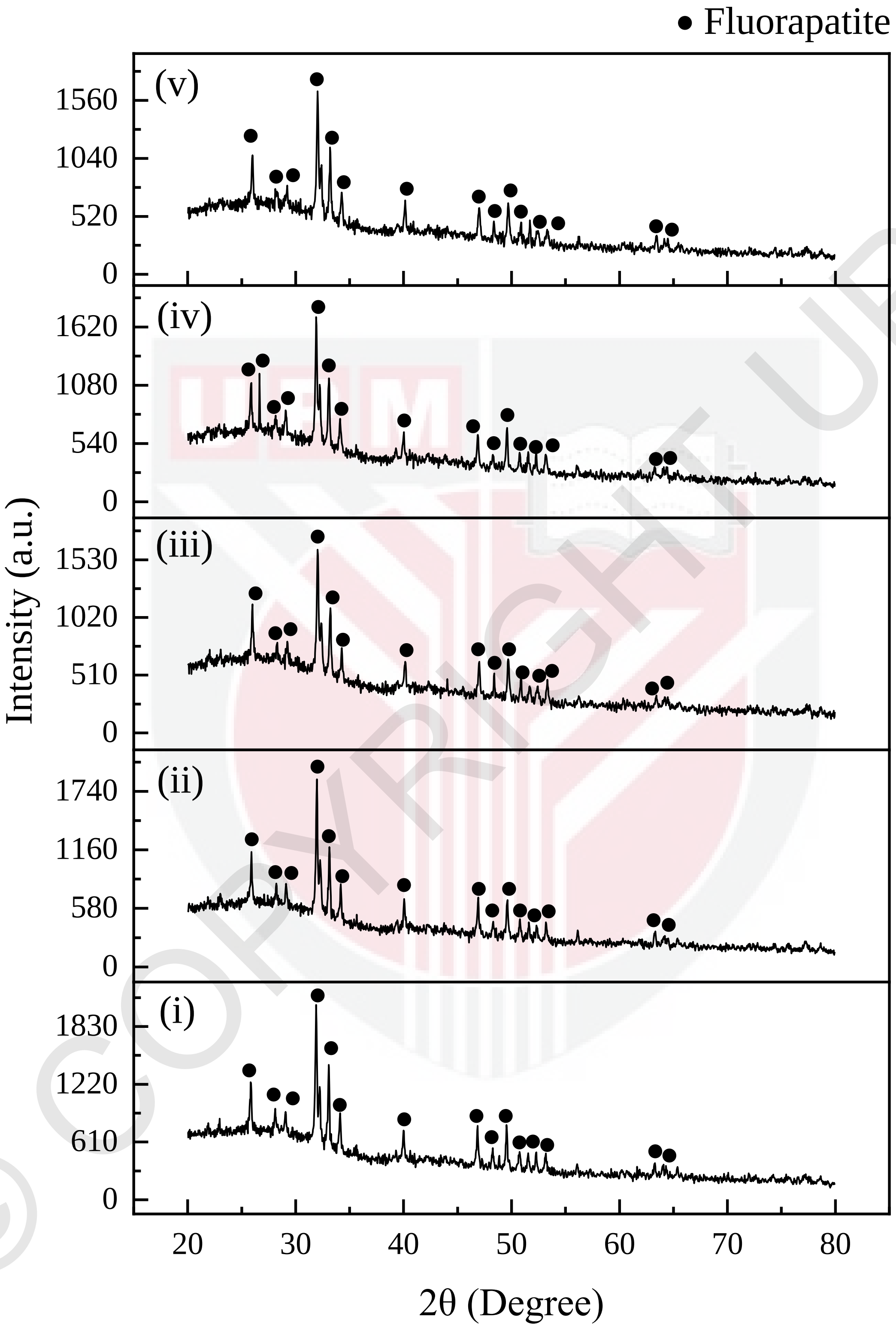


Figure 4.3: XRD pattern of GIC with 0 wt.% of HA sample at (i) 1 day, (ii) 7 days, (iii) 14 days, (iv) 21 days and (v) 28 days of ageing times

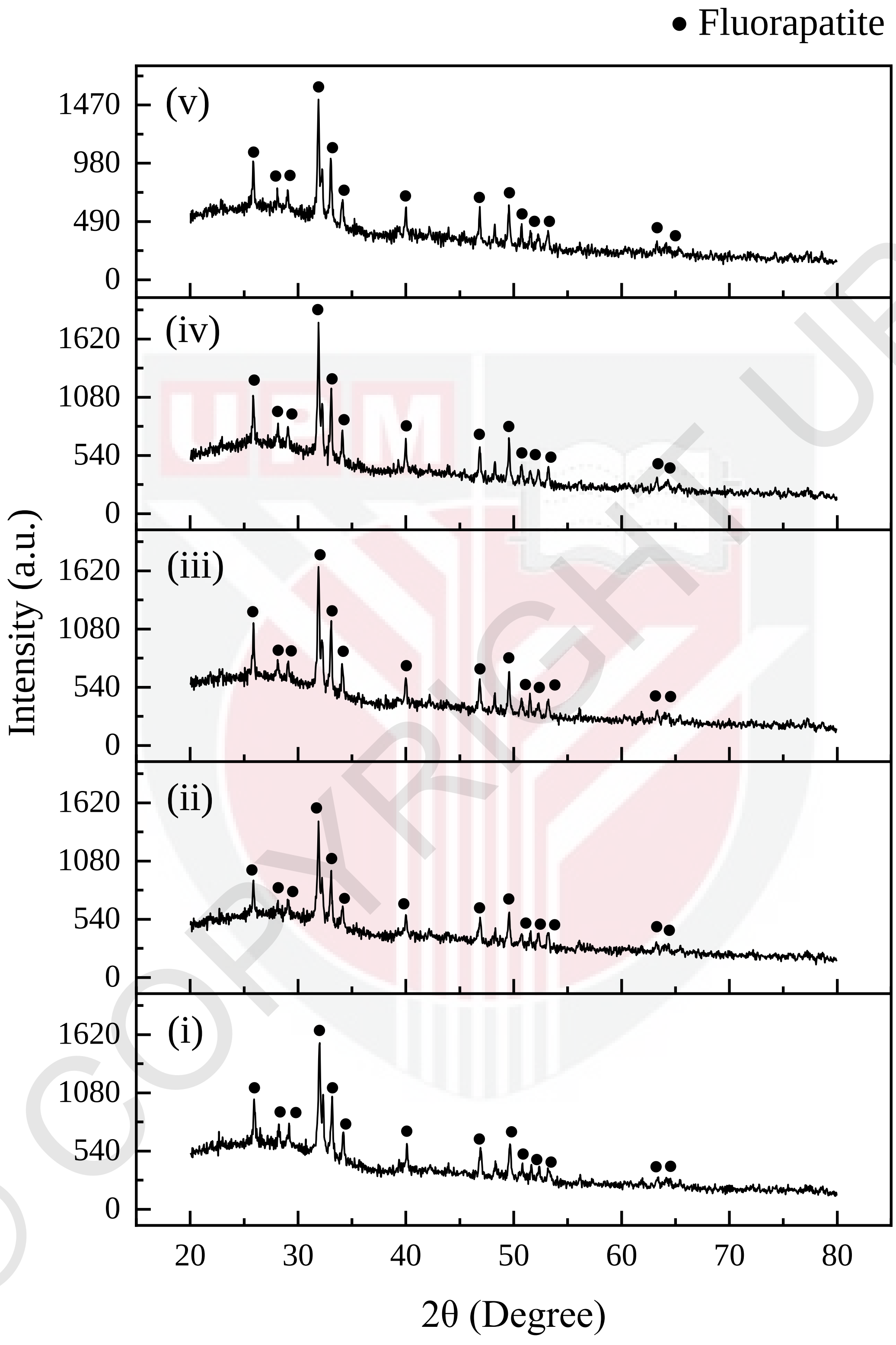


Figure 4.4: XRD pattern of GIC added with 1 wt.% of HA sample at (i) 1 day, (ii) 7 days, (iii) 14 days, (iv) 21 days and (v) 28 days of ageing time

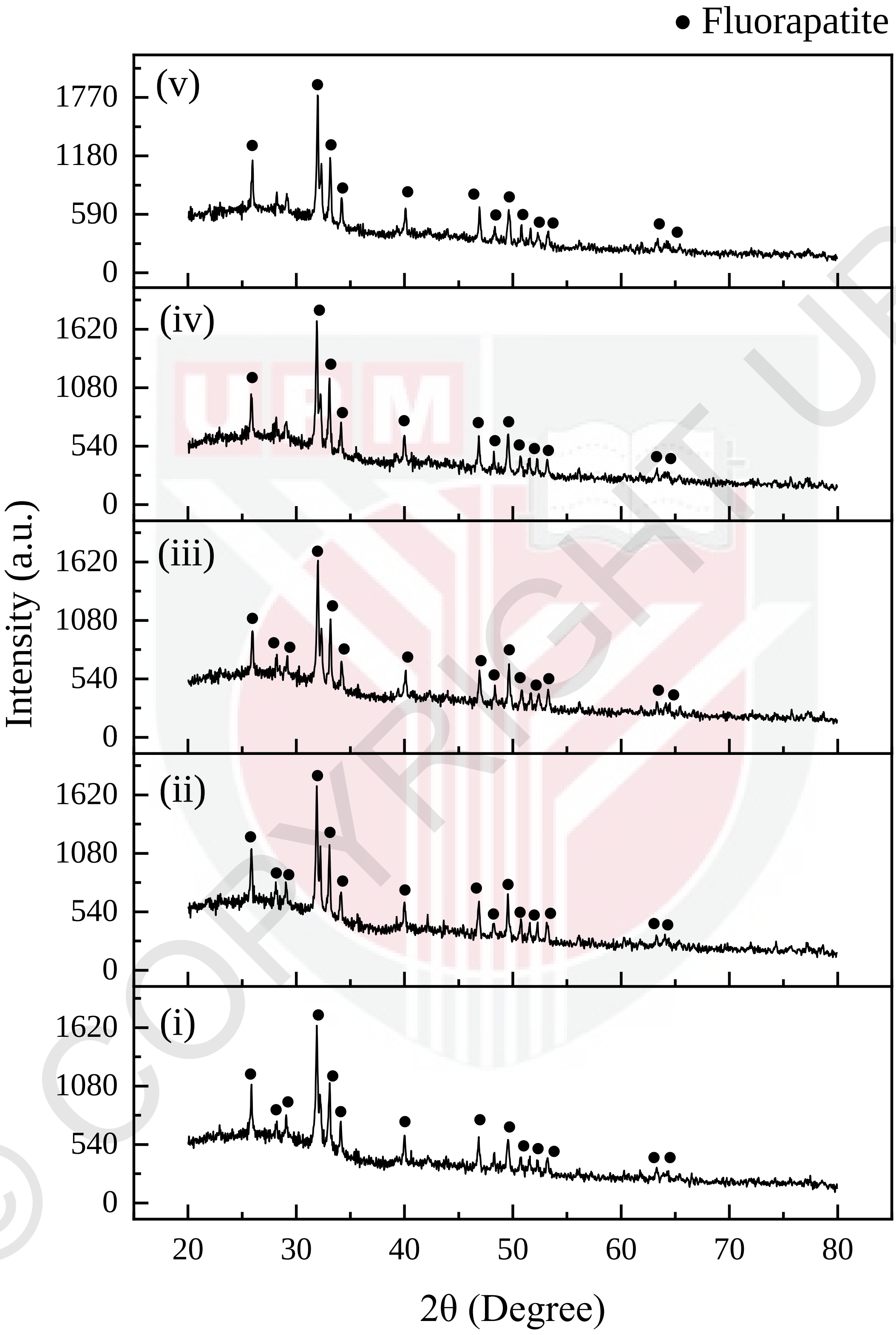


Figure 4.5: XRD pattern of GIC added with 2 wt.% of HA sample at (i) 1 day, (ii) 7 days, (iii) 14 days, (iv) 21 days and (v) 28 days of ageing time

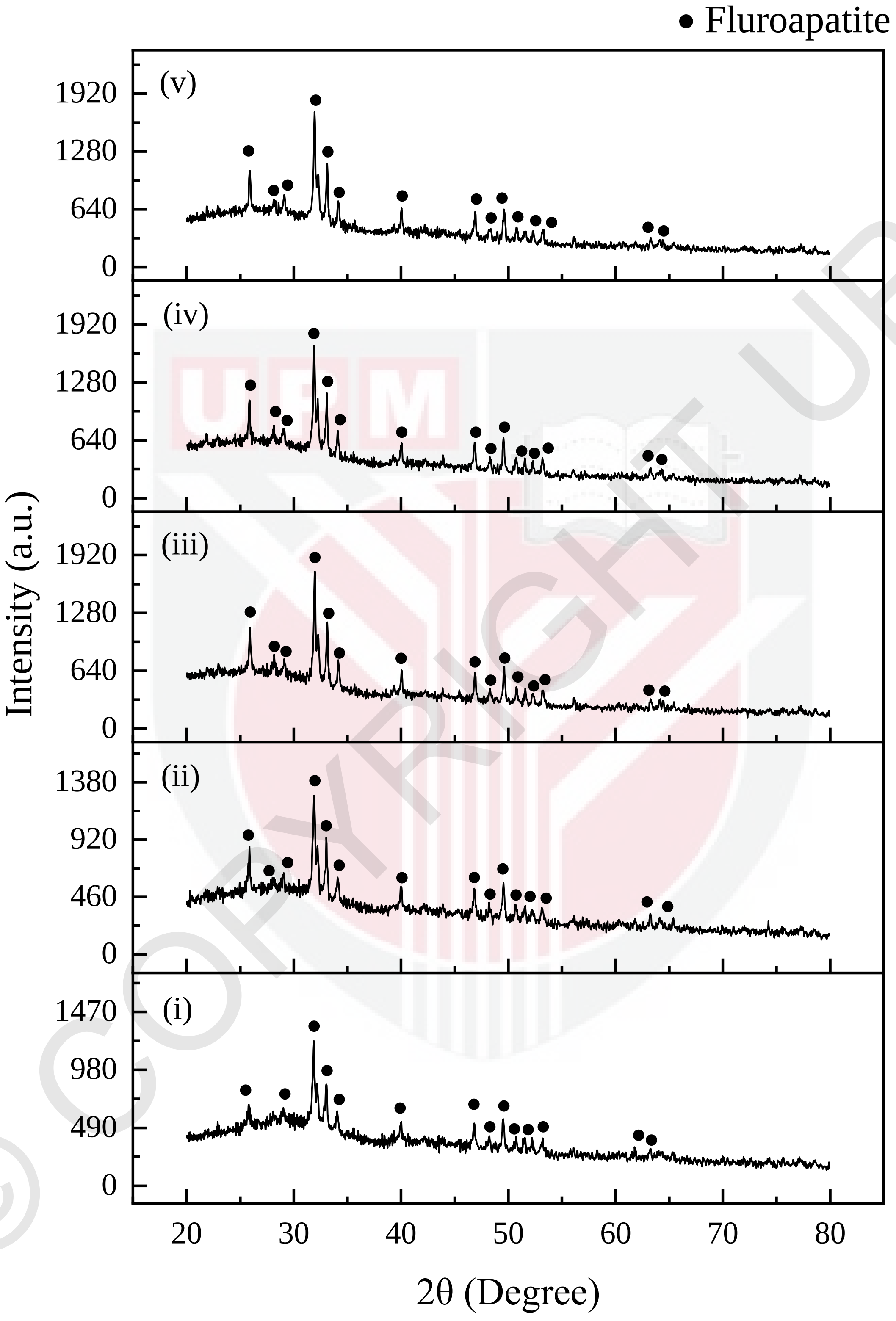


Figure 4.6: XRD pattern of GIC added with 3 wt.% of HA sample at (i) 1 day, (ii) 7 days, (iii) 14 days, (iv) 21 days and (v) 28 days of ageing time

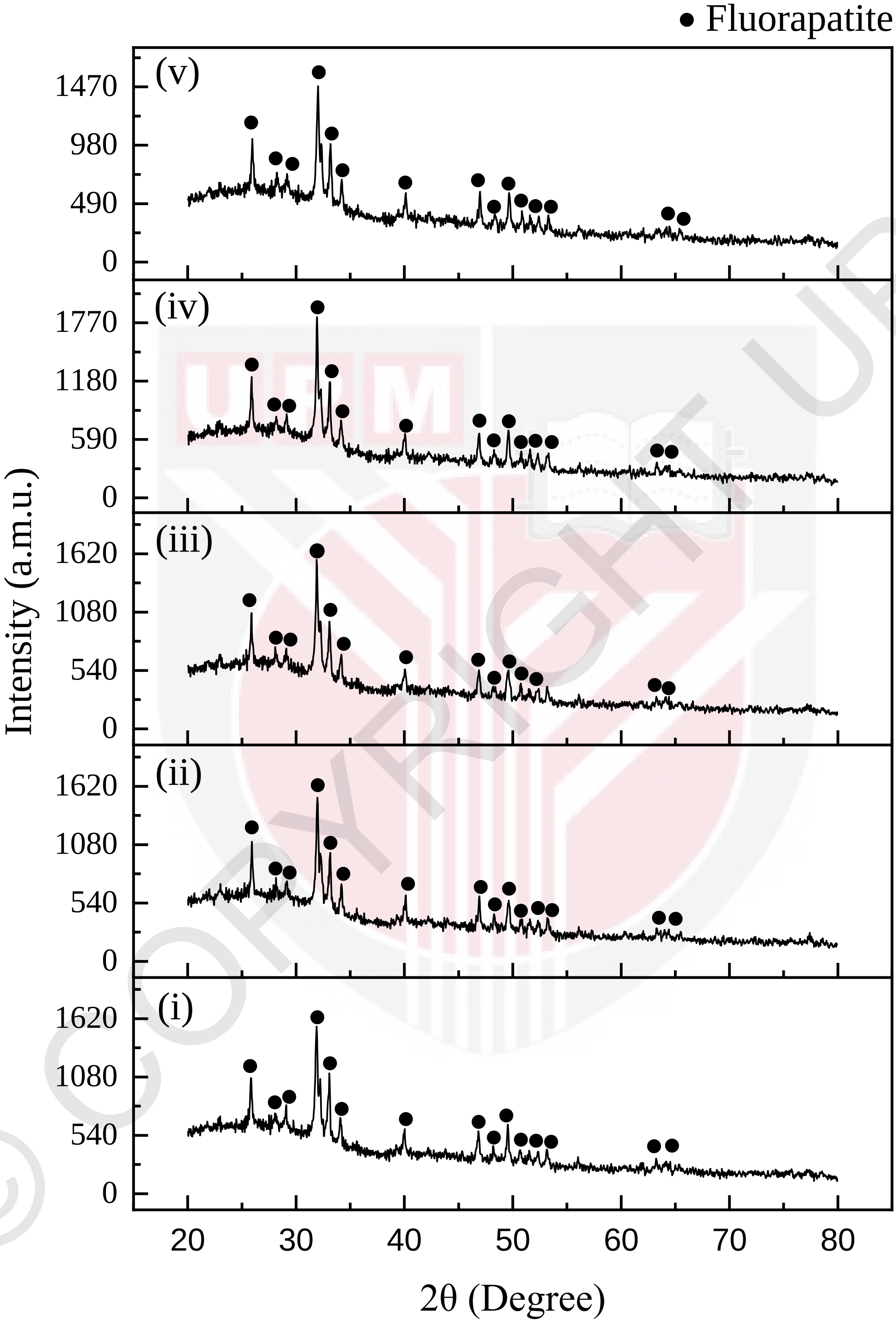


Figure 4.7: XRD pattern of GIC added with 4 wt.% of HA sample at (i) 1 day, (ii) 7 days, (iii) 14 days, (iv) 21 days and (v) 28 days of ageing time

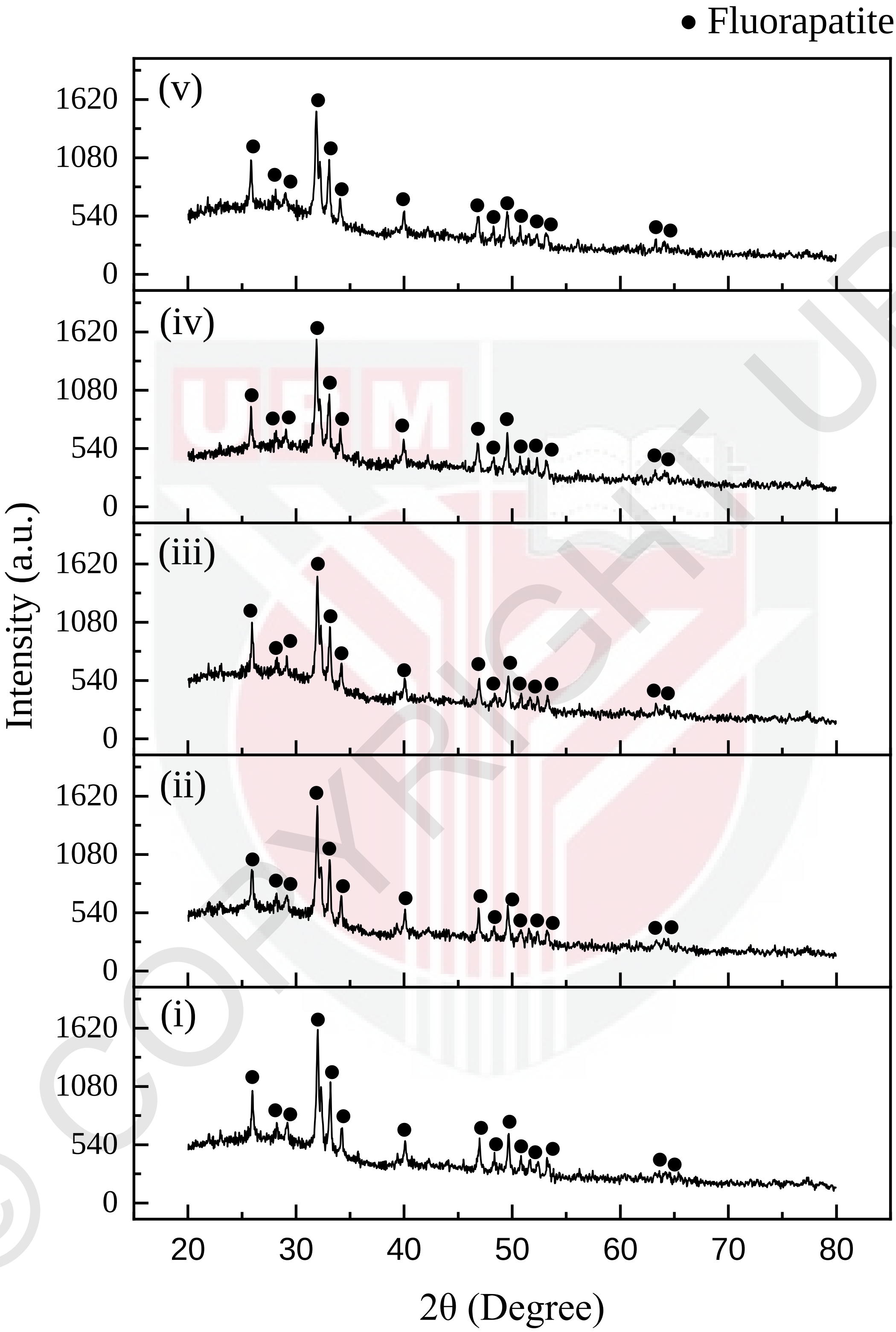
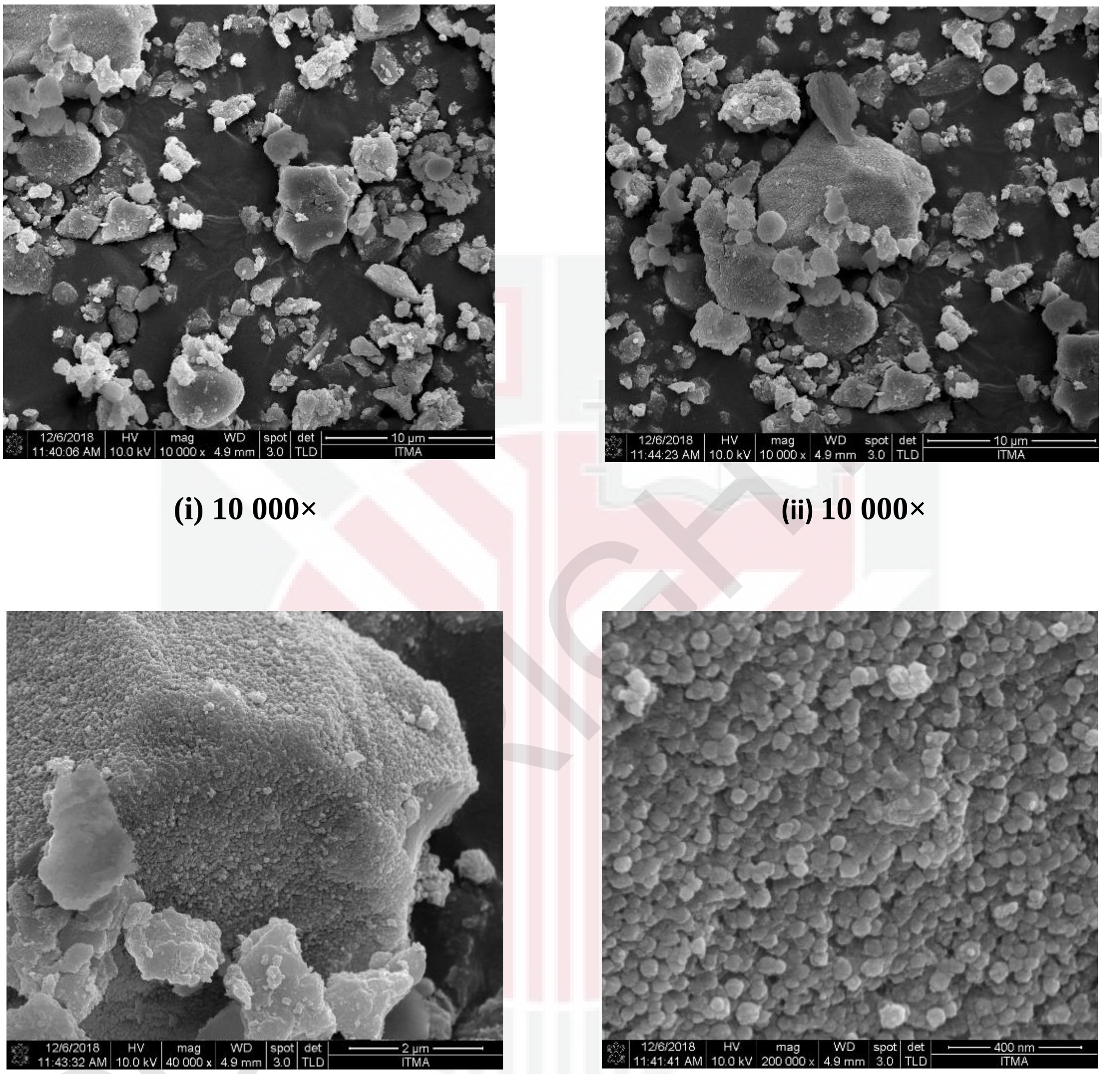


Figure 4.8: XRD pattern of GIC added with 5 wt.% of HA sample at (i) 1 day, (ii) 7 days, (iii) 14 days, (iv) 21 days and (v) 28 days of ageing time

4.4 Field Emission Scanning Electron Microscopy (FESEM)

In this section, the morphology and microstructure of the GIC samples were analyzed and observed by using FESEM analysis. The microstructure image of the GIC samples were presented in Figure 4.9 (i), (ii), (iii) and (iv) under different magnification. Based on the FESEM image of the GIC samples, it is noticed that different magnification results in different illustration of the morphology and microstructure. Figure 4.9 below show the image of FESEM analysis of GIC samples without the addition of HA at 7 days of ageing time.

Based on Figure 4.9 (i) and (ii), the microstructure of the GIC samples existed as a non-uniform particle distribution with irregular shape. The irregular shape of the particle indicated some granular structure, indicating that the particle was a glass type which is from the usage of ASF glass powder in the GIC formulation. A clump of spherical shaped particles was detected on the glass particle which is known as apatite. The structure that existed on the control GIC samples was observed at a higher magnification of FESEM to produce another microstructure images. FESEM images of GIC samples were observed under magnifications of 40 000× and 200 000× in Figure 4.9 (iii) and (iv) respectively. A rod or needle-like particles from apatite crystals were visible in the photos, particularly in Figure 4.9. (iii). The particles appear to clump together on the glass surface, and some agglomerated spherical particles were found in the samples, indicating that apatite particles are present in the GIC formulation.



(i) 10 000× **(ii) 10 000×**

(iii) 40 000× **(iv) 200 000×**

Figure 4.9: FESEM microstructure of GIC at different magnification of (i) 10 000×, (ii) 10 000×, (iii) 40 000× and (iv) 200 000× at 7 days of ageing time

CHAPTER 5

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

In this study, ASF glass powder with composition represented by a formula of $25SLS\text{-}15CS\text{-}20CaF_2\text{-}20P_2O5\text{-}20Al_2O_3$ was prepared from melt-quench technique. The ASF glass powder were then mixed together with different composition of HA and were mixed with water using 3:1:1 ratio in order to produce GIC before underwent various ageing time.

Based on physical and structural features, the impact of adding HA to GIC formulation at different ageing times was investigated. Density results of GIC samples showed an increment as HA powder was introduced into GIC formulation. As the HA powder was included into the GIC formulation, some density findings of GIC samples showed a significant increase. The addition of a high concentration of HA content to the GIC samples, resulted in a decrease in density trend and inconsistent density values. For example, the addition of 5% HA to the GIC formulation caused the density trend to decrease after 7 days of ageing time. Furthermore, ageing time plays a crucial impact in the increment of density values for GIC samples.

FTIR analysis showed that the GIC samples contains a variety of band and stretching vibrations such as O–P–O bending mode, asymmetric P-O stretching mode, C–O vibration mode, asymmetric COOH mode, and OH vibration mode. As a result, it has been proven that the GIC samples contained the band and stretching vibrations were within the GIC samples subjected to different ageing time process. Furthermore, XRD analysis of the GIC samples revealed a glassy structure and amorphous phase with small, sharp peaks and humps, which are known as fluorapatite.

Meanwhile, a FESEM analysis of a GIC sample without the addition of HA after 7 days of ageing demonstrated a non-uniform particle distribution, irregular morphologies, and random grain size of the samples. The presence of agglomerations of spherical and needle-like particles in the samples shows that apatite crystals were present.

Finally, research on the benefits of adding fillers such as HA to GIC formulations can significantly improve the physical, structural, and mechanical properties of the cement. The potential use of GIC cement with HA in dental applications, especially as a restorative material, is highly useful and advantageous.

5.2 Suggestion on the future works

In this research, the study on the effect of adding HA into GIC can be improved for potential application in dental application by these suggestions as follows:

1) Different ratio of Glass:PAA:H_2O can be used in fabricating GIC samples.
2) Use different filler incorporated to the GIC samples such as graphene and strontium.
3) Mechanical testing must be done in order to obtain better information on mechanical properties of the sample eg: Vickers hardness, fracture toughness and diametral tensile strength.

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APPENDICES

PREPARATION OF ASF GLASS

Weighing and milling

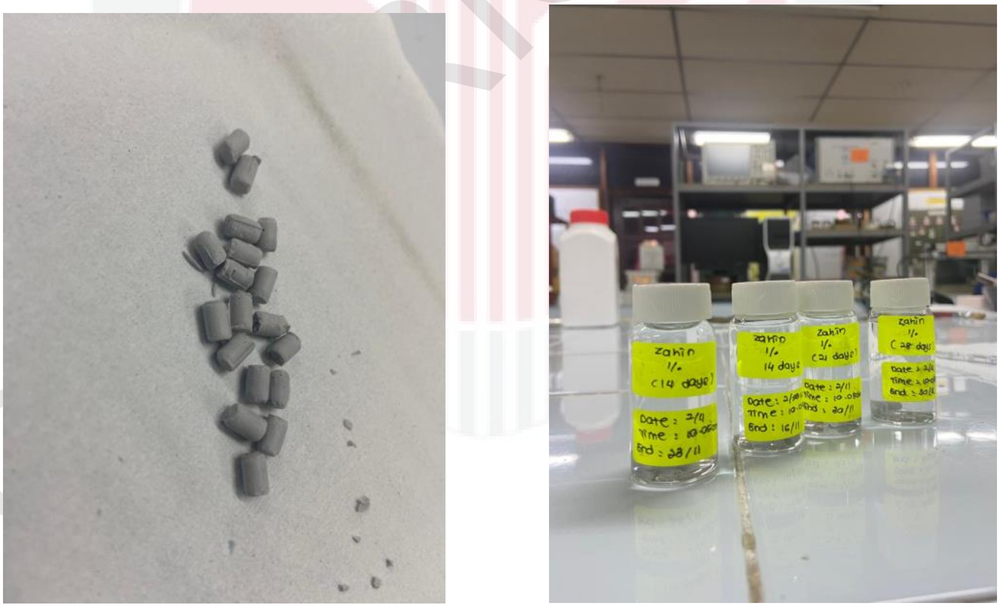
Melting and water quenching process

Crushing using plunger from ASF glass frits

Grinding and sieving

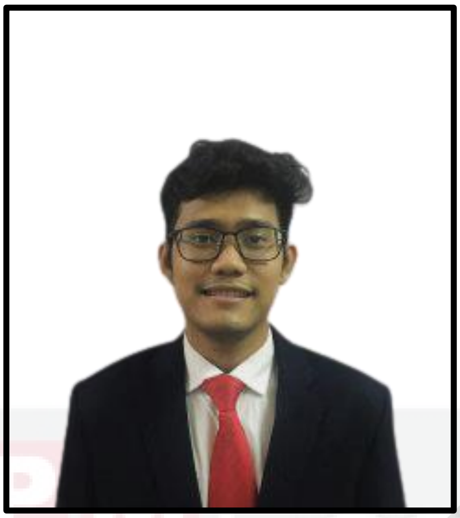
PREPARATION OF GIC

Setting reaction of GIC samples



GIC samples soaked in deionized water for ageing process

VITAE



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