
**UNIVERSITI PUTRA MALAYSIA**

***EFFECT OF SINTERING TEMPERATURES ON PHYSICAL AND STRUCTURAL PROPERTIES OF GLASS IONOMER CEMENT DERIVED FROM ASF BASED GLASS CERAMICS***

**FARAH NADHIRAH BINTI MOHD YUNUS**

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**BY**

**FARAH NADHIRAH BINTI MOHD YUNUS**

**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 Md. Shuhazlly Mamat 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 SINTERING TEMPERATURES ON PHYSICAL AND STRUCTURAL PROPERTIES OF GIC DERIVED FROM ASF BASED GLASS CERAMICS**

by

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February 2022

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Glass ionomer cement (GIC) is a common restorative substance used in dentistry, particularly for restorative and luting purposes. However, research on the use of Alumino-Silicate-Fluoride (ASF) based glass ceramics produced from waste materials in the manufacture of GIC is restricted. This research's main focus is to produce GIC using ASF based glass ceramics derived from CS and SLS waste materials for calcium and silica sources. GIC was fabricated using three main components of ASF based glass ceramics, polyacrylic acid (PAA) and water based on 3:1:1 ratio. Density measurements, X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Field Emission Scanning Electron Microscopy (FESEM) were used to assess the physical and structural properties of GIC. The density measurement of GIC increased from Room Temperature (RT) to 600 °C. At a high sintering temperature of 700-900 °C, the density then decreased.

The highest density measurement of GIC is 1.844 g/cm$^3$ which is at 600 °C with ageing time of 21 days while the lowest density measurement of GIC is 1.585 g/cm$^3$ which is at 900 °C with ageing time of 1 day. This is because at high sintering temperatures, anorthite ($Ca(Al_2Si_2O_8)$) and mullite ($Al_5SiO_{9.5}$) formed. Next, FTIR revealed the presence of $v_4$ O-P-O bending mode, C-O bond properties, $v_3$ asymmetric P-O stretching, C-O, and OH vibration modes. The presence of the crystal phase was confirmed by FTIR, which detected OH chemical bonding around 3400 cm$^{-1}$ in the spectrum wavenumber. The development of spherical particles and agglomerated needle-like apatite crystals is revealed by FESEM morphology. In FESEM, a homogeneous spherical microstructure was discovered, which devitrified to a coarse structure at high sintering temperatures. Overall, the ASF glass ceramics samples made from waste materials were shown to be a high potential candidate for dental application.

## ABSTRAK


**KESAN SUHU PENSITERAN TERHADAP SIFAT FIZIKAL DAN STRUKTUR GIC DIHASILKAN DARI SERAMIK KACA BERASASKAN ASF**

Oleh

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Simen ionomer kaca (GIC) ialah bahan pemulihan yang biasa digunakan dalam pergigian, terutamanya untuk tujuan pemulihan dan proses rekat. Walau bagaimanapun, penyelidikan mengenai penggunaan seramik kaca berasaskan Alumino-Silicate-Fluoride (ASF) yang dihasilkan daripada bahan buangan dalam pembuatan GIC adalah dihadkan. Fokus utama penyelidikan ini adalah untuk menghasilkan GIC menggunakan seramik kaca berasaskan ASF yang diperoleh daripada bahan buangan CS dan SLS untuk sumber kalsium dan silika. GIC telah difabrikasi menggunakan tiga komponen utama seramik kaca berasaskan ASF, asid poliakrilik (PAA) dan air berdasarkan nisbah 3:1:1. Pengukuran ketumpatan, pembelauan sinar-X (XRD), Spektroskopi Inframerah Transformasi Fourier (FTIR), dan Mikroskopi Elektron Pengimbasan Pancaran Medan (FESEM) digunakan untuk menilai sifat fizikal dan struktur GIC. Pengukuran ketumpatan GIC meningkat daripada suhu bilik hingga 600 °C. Pada

suhu pensinteran tinggi 700-900 °C, ketumpatan kemudiannya berkurangan. Ini kerana pada suhu pensinteran yang tinggi, anorthite ($Ca(Al_2Si_2O_8)$) dan mullite ($Al_5SiO_{9.5}$) terbentuk. Seterusnya, FTIR mendedahkan kehadiran mod lenturan O-P-O $v_4$, sifat ikatan C-O, regangan P-O asimetri $v_3$, mod getaran C-O dan OH. Kehadiran fasa kristal telah disahkan oleh FTIR, yang mengesan ikatan kimia OH sekitar 3400 $cm^{-1}$ dalam nombor gelombang spektrum. Perkembangan zarah sfera dan kristal apatit seperti jarum terkumpul didedahkan oleh morfologi FESEM. Dalam FESEM, struktur mikro sfera homogen ditemui, yang terdevitrif kepada struktur kasar pada suhu pensinteran yang tinggi. Secara keseluruhannya, sampel seramik kaca ASF yang diperbuat daripada bahan buangan telah ditunjukkan sebagai calon berpotensi tinggi untuk aplikasi pergigian.

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## APPROVAL

This thesis entitled "Effect of Sintering Temperatures on Physical and Structural Properties of GIC derived from ASF Based Glass Ceramics" by Farah Nadhirah Binti Mohd Yunus (Matric No.: 196235), 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**

I hereby confirm that:

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| GIC | Glass ionomer cement |
| PAA | Polyacrylic Acid |
| HA | Hydroxyapatite |
| CS | Clam Shells |
| SLS | Soda Lime Silicate |
| ASF | Alumino-silicate-fluoride |
| FA | Fluorapatite |
| PMMA | Polymethylmethacrylate |
| $\sigma$ | Tensile Strength |
| XRD | X-ray Diffraction Spectroscopy |
| FTIR | Fourier transform infrared spectroscopy |
| FESEM | Field emission scanning electron microscopy |
| $T_c$ | Crystallization temperature |
| $T_m$ | Melting point |

# CHAPTER 1
# INTRODUCTION

## 1.1 Introduction to Glass Ionomer Cement

Biomaterials are products used in medical, dental, veterinary, or pharmaceutical applications that come into intimate, long-term contact with body tissues, usually by being inserted within them. A biomaterial is a non-viable substance used in a medical device that is designed to interact with biological systems, according to a recent conference dedicated to defining those concepts. Hip replacements, contact lenses, and intraocular lenses are all well-known examples (Wan Jusoh et al., 2021).

Since the body is so well prepared to resist any intruding substance, whether it is a bacterium or a splinter of wood, the products that have any hope of succeeding inside this aggressive and responsive environment must be able to overcome these obstacles. The setting must be carefully selected. Biomaterials is an almost unprecedented combination of physical and biological sciences, and it is becoming increasingly necessary to bring these elements together to aid in the production of high-quality biomaterials that can function optimally in this setting (Williams, 1987).

Biomaterials play an essential role in biomedical research, to the best of our knowledge, because they can interact successfully with biological systems. Researchers are still working to improve the quality and outputs of biomaterials in the biomedical area due to their unique characteristics and wide range of applications (Williams, 1987). GIC is a form of biomaterial that has been used in clinical settings. In this study, five chemical

compounds were used for glass composition to manufacture bioglass, also known as alumino-silicate-fluoride, in order to prepare GIC (Smith, 1990). Bioglass has been a promising candidate for biomaterial formulation in orthopaedic and dental applications due to its antibacterial and mechanical properties. One of the first to use the $SiO_2$-CaO-$CaF_2$-$P_2O_5$-$Al_2O_3$ composition is the alumino-silicate-fluoride (ASF) based bioglass with fluoride (Jalil et al., 2020).

Bioglass is important to biomaterials research because it is one of the synthetic materials that can smoothly bind to bone. Bioglass is a bioactive glass made up of the same proportions of calcium and phosphate as hydroxyapatite in bone. This glass is biocompatible and binds to the tissue (Thoo et al., 2013). Meanwhile, bioactivity is defined as the ability of a biomaterial's surface to generate tissue, resulting in a mechanically solicitable interface. Clam Shells (CS), Soda Lime Silicate (SLS), $CaF_2$, $P_2O_5$, and $Al_2O_3$ are all used to make ASF bioglass, according to the empirical formula [$xCS\cdot(45-x)SLS\cdot15CaF_2\cdot20P_2O_5\cdot20Al_2O_3$] , where x = 1, 2, 3, 4 and 5 (wt.%).

CS and SLS were the waste materials used to make ASF bioglass (Khiri et al., 2020). In the field of stomatology, bioactive glass ceramics are extensively utilized in two ways which are as implants to hold dentures in place and in the fabrication of dentures (Sidhu & Nicholson, 2016).

Bioglass dentures outperform previous materials in terms of appearance, biological compatibility, mechanical strength, and durability. Because these substances have the ability to replace teeth and any bone that may be present naturally, both bioactive and inert compounds are employed to preserve excellent biological compatibility (Thoo et al., 2013).

Because of its better compressive strength, corrosion resistance, and low density and weight, bioglass is the best option these days.

This research gives a detailed comprehension of the interaction between bioglass structures and physical efficiency, as well as knowledge of potential biomaterials for fabrication, such as GIC (Rahman et al., 2019). In the utensil, bioactive materials, and construction industries, SLS glass is extensively utilized. Furthermore, Anadara Granosa, commonly known as CS, has emerged as a possible candidate for the preparation of dental applications (Jalil et al., 2020).

## 1.2 Problem Statement

Solid waste is one of Malaysia's main environmental issues, with approximately 18,000 tonnes of rubbish discharged each day. According to estimates, Peninsular Malaysia will discard more than 30,000 tonnes of solid garbage every day by 2020 (Khiri et al., 2020). First, according to Wan Jusoh (2019), GIC has been shown to have physical and structural properties to be used in dental material. Varying the ageing time and sintering temperatures is thought to improve the physical and structural properties of GIC. As a result, the presence of strontium fluoride phosphate ($Sr(PO_4)_3F$) and mullite ($Al_6Si_2O_{13}$) after heat treatment is predicted to address this problem. This research aims to develop the GIC's physical, structural, and mechanical properties in order to keep up with industry developments and satisfy a variety of aesthetic and functional requirements. Problems stated will be discussed more on subtopic 1.4 which is Significance of Study.

## 1.3 Research Objectives

Based on the problem statements above, the objectives for this study were:

1. To produce GIC from ASF-based glass ceramics made from CS and SLS waste materials as calcium and silica sources.
2. To investigate on how different sintering temperatures affect GIC's physical and structural properties.
3. To analyze the physical and structural properties of GIC after various ageing times.

## 1.4 Significance of Study

The goal of this study was to produce GIC out of ASF-based glass ceramics made from CS and SLS waste. To accomplish distinct phase transformations, ASF-based glass ceramics are sintered using a controlled sintering process. In the field of dentistry, phase change of ASF-based glass ceramics is important. The two main phases of glass and glass ceramics are amorphous and crystalline structures, with each phase expected to provide significant benefits in the field of dentistry (Jusoh et al., 2019). The use of ASF-based glass ceramics is expected to improve GIC's performance and characteristics. Through changes in glass crystallinity, the sintering process used in this work can transform ASF glass into glass ceramics.

Glass, deionized water, and polymeric acid are all used in the polymerization process to create GIC (Thoo et al., 2013). The GIC is widely used in dental applications such as luting cement, restorative materials, and sealants (Moheet et al., 2018). This is because of their superior adhesion, biocompatibility, and aesthetic appearance. However, researchers are working to improve the mechanical strength of GICs, which is one of its

major drawbacks. The difference in GIC sintering temperature and ageing times was predicted to lead to the mechanical characteristics of GIC being improved. As a result, the study should achieve the main goal of this research, which is to improve the mechanical characteristics of the GIC.

Some innovative waste management methods, such as transforming waste into useful resources for the industrial market, have been introduced to utilize and improve waste management. Due to its high mineral composition, food waste can be utilized as a raw material in the manufacture of glass, glass ceramics, and ceramics (Cornejo et al., 2014). CS and SLS are two examples of food waste that may be used in the industrial market. CS and SLS waste glass are examples of food waste that can be used in the industrial market.

According to previous studies, CS waste glass has a calcium oxide composition of more than 90%, whereas SLS waste glass has a silicon dioxide composition of 70% (Fritz & Elsner, 1998). In ASF fabrication, waste materials from CS and SLS glass are used to produce CaO and $SiO_2$ compositions. In research, the use of waste in the manufacture of GIC is limited. As a result, this research is being carried out to determine the efficacy of waste in the GIC.

## 1.5 Overview of Thesis

The following is how the study is structured and organized. In Chapter 1, biomaterials, bioceramics, GIC, issue statements, work goals, research scope, and importance will be learnt. In Chapter 2, previous work relevant to current research is reviewed, with an emphasis on research performed with different sintering temperatures and ageing times of GIC made from waste materials. The methodology, which includes sample preparation, characterization, and analysis, is outlined in Chapter 3. In Chapter 4, particular instruments are used to study and discuss the impact of various sintering temperatures and ageing times on the physical and structural properties of GIC. Finally, in Chapter 5, the conclusion and future work recommendations are discussed.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

Chapter 2 consists of review on the previous research of the ASF based glass ceramics and GIC. This chapter provides similar findings regarding this research and some previous research information related to this project. The findings obtained were used as a guiding principle throughout this research.

## 2.2 Biomaterials

Biomaterials are biological substances that are used in the human body or in medical devices. Because of its properties, which include an apatite phase that is similar to Hydroxyapatite, the most abundant mineral in the human body, it was created to interact with biological systems (Khalid et al., 2017). Biomaterials can also be identified by four characteristics which are biocompatibility, biodegradability, bioactivity, and bioinert (Kaur et al., 2014).

45S5 Bioglass® is a first-generation biomaterial made of $45SiO_2$-$24.5Na_2O$-$24.5CaO$-$6P_2O_5$ (wt.%) glass (Fernandes et al., 2018). The bioactive capabilities of bioglass and the high reactivity of the surface material were demonstrated in this composition (Khalid et al., 2017). This demonstrates that bioglass is one of the most successful biomedical technologies.

### 2.2.1 ASF Based Glass Ceramics

Fluoride is present in ASF-based glass ceramics, and it is one among the first products with the $SiO_2$-CaO-$CaF_2$-$P_2O_5$-$Al_2O_3$ composition. In the bioglass composition, the presence of CaO promotes the production of crystalline phases. Moreover, as silica has the highest percentage of glass constituents, it is added to bioglass compositions and serves as the backbone in dental ceramics applications (El-Meliegy and Van Noort, 2011). The production of crystalline phases is crucial in dental ceramic applications, which provide properties similar to Hydroxyapatite mineral phases in biological systems (Rahman et al., 2019).

$CaF_2$ fluoride ions are utilized to characterize glass behaviour because they can change the nature of glass, allowing it to be used in dental and medical applications (Hill et al., 2006; Rabiee et al., 2015). The presence of $P_2O_5$ in the ASF composition is similar to the $CaF_2$ function, in which it works as a nucleating agent (Mukherjee et al., 2013). $Al_2O_3$, on the other hand, has been used in orthopaedics for about 20 years due to its low coefficient of friction and negligible wear (El-Meliegy & Van Noort, 2011).

ASF bioglass is costly to manufacture from pure $SiO_2$ and CaO, and glass synthesis requires a high melting temperature. Recycled SLS glass and CS will be used as $SiO_2$ and CaO sources to solve the problem, reducing the price of ASF bioglass production (Rahman et al., 2019). In this research, some components in ASF bioglass with a composition of silica, aluminium, and fluoride were substituted with SLS glass and CS vitreous waste material (Jusoh et al., 2019). SLS glass can be used as a source of silica in ASF bioglass formulations for dental applications because its principal chemical compositions are $SiO_2$ (60-75%) and CaO (5-12%). SLS glass and CS are projected to have outstanding

mechanical and optical properties, including high thermal stability, high transparency, and a low melting point (Thoo et al., 2013).

Because of the high percentage of silica in the glass composition, SLS glass was utilized in the GIC. The absence of a strong peak in the XRD study demonstrates the nature of the SLS glass in the GIC composition (Thoo et al., 2013). Furthermore, from the previous study of Thoo et al. (2013), FTIR analysis reveals a good establishment of the cross-linking reaction, despite the fact that the reaction was slower in the beginning than the GIC with pure silica. The compressive strength also exhibits a positive pattern, with strength increasing over time. The SLS glass emerged as a potential candidate in the GIC composition as a result of the research (Rahman et al., 2019).

## 2.3 Glass Ionomer Cement (GIC)

Glass ionomer cements (GIC) were developed as a result of research into dental silicate cements in the late 1970s. GICs are used in a range of dental procedures, such as root canals and tooth restoration. They have a variety of benefits over bone cements based on polymethylmethacrylate (PMMA) (Jalil et al., 2020). Good tooth adherence, less toxic effect on dental pulp, continuous fluoride release, and lack of exothermic polymerization are only a few of them. GICs' excellent adhesive properties, as well as their fluoride release, help to reduce the rate of secondary caries in both filled teeth and adjacent teeth's enamel surfaces (Gu & Fu, 2004).

A glass powder made of calcium fluoroalumino-silicate and an aqueous solution of a poly(acrylic acid-itaconic acid) copolymer containing tartaric acid were combined to

make GIC (Smith, 1998). Glass ionomers are used to restore teeth that have been affected by caries or other forms of decay (Nicholson et al., 2020). Further advancements have resulted in their widespread use as class V restorations for cervical abrasion and erosion lesions, root caries, luting cements, liners and bases, core build-up materials, fissure sealants, tunnel preparations, temporary repairs of fractured teeth or deficient crown edges, and luting agents for orthodontic brackets, among other uses (Rafeek, 2008).

GIC has attractive properties that make it a good option for clinical use especially in dentistry. GIC by conventional acid base neutralization reaction have a better physical properties rather than the self-hardening glass ionomer cement (Wan Jusoh et al., 2021). Special basic glass powders incorporating phosphate and sodium salts, such as calcium or strontium alumino-fluoro-silicate, are used to make glass ionomers (Khiri et al., 2020). GIC is made up of three ingredients which are glass powder, water, and polyacid. These can form salts when combined with a polymeric water-soluble acid solution, thereby crosslinking the polymer chain and hardening the material. Glass ionomers are brittle, with compressive strengths ranging from 150 to 220 MPa (Smith, 1990). GIC with nanoparticles were shown to be easier to mix and to have less air gaps and internal micro cracks than those without nanoparticles (Wan Jusoh et al., 2021).

The researchers used a range of nanoparticles, including titanium oxide nanotubes and nanoparticles. All of these properties contribute to the observed increase in compressive strength (Nicholson et al., 2020). It would be ideal if GIC could be used to create fluoride-releasing inlays and onlays that cling to tooth tissue. GIC is a siliceous hydrogel enveloped by a calcium and aluminium polyacrylate matrix with glass particles implanted. The structure of the set GIC has excellent adherence to enamel and dentine, as

well as cariostatic qualities due to the long-term release of fluoride (Jalil et al., 2020). The initial lack of strength of GIC makes it unsuitable for incisal edge repair, marginal ridge restoration, or use as an inlay/onlay material like composite resins or porcelain (Rafeek, 2008).

GIC is less technically demanding than resin-based composites and does not imitate tooth colour as well as composites. However, it may perform better in many aspects than resin-based composites because it is less technically demanding (Wilson, 1989). It is crucial to remember that glass ionomer is an inorganic substance that can be eroded by acids. Studies have shown that when used in high-risk areas, conventional glass-ionomers can seriously erode. Furthermore, excessive soft drink consumption may negatively impact conventional glass-ionomer restorations (Gu & Fu, 2004).

## 2.4 Components of GIC

GIC is made up of three components which are polymeric water-soluble acid, basic (ion-leachable) glass, and water. As a result, ASF glass, polyacrylic acid (PAA), and deionized water are used in this project.

### 2.4.1 Glass

Clam Shells (CS), Soda Lime Silicate (SLS), $CaF_2$, $P_2O_5$, and $Al_2O_3$ are used in the manufacturing of ASF bioglass, using the empirical formula $[xCS\cdot(25-x)SLS\cdot20CaF_2\cdot20P_2O_5\cdot20Al_2O_3]$ , where x = 1, 2, 3, 4 and 5 (wt.%) according to Rohaniah's research. CS and SLS were the waste ingredients used to make ASF bioglass. The addition of CaO to the glass composition aids in the formation of the crystalline phase

(Khiri et al., 2020). Apart from that, in order for bioglass materials to interact effectively with real bone tissue or teeth, the apatite phase $Ca_3(PO_4)_2$ must be present, as it is a component of natural bones and gives strength as well as the potential to grow (Sidhu & Nicholson, 2016).

Following that, because of its increased compressive strength, excellent corrosion resistance, and low density and weight, bioglass is currently the preferable material (Thoo et al., 2013). This research contributes to a thorough understanding of how bioglass structures relate with physical performance, as well as knowledge for the development of future biomaterials such as GIC (Rahman et al., 2019). GIC glass ceramics made of alumino-silicate-fluoride are thought to have good properties and are suitable for dental application. The use of waste materials as replacements for silicate and calcite sources, such as CS and SLS glass, can lower production costs while simultaneously addressing environmental concerns (Jalil et al., 2020).

The existence of fluorapatite (FA) in the ASF glass ceramics composition can have an impact on the properties of the resulting cement. As a result, GIC manufactured with ASF glass ceramics as the base silicate powder was found to be mechanically insufficient, restricting its application in dentistry (Wan Jusoh et al., 2021). Glass development in medical applications is widely accepted, particularly in dentistry and orthopaedics. The inclusion of fluoride in the glass system can improve its mechanical strength. It can also work as an antibacterial agent by releasing fluoride ions in an acidic environment such as that produced by bacteria in the mouth (Klos et al., 2020).

GIC has been identified as the most advantageous and appropriate material for usage in dental applications when compared to other materials (Wilson, 1989). As a result,

various investigations on GIC linked to altering glass phases are needed to improve GIC properties, specifically mechanical features such as hydroxyapatite, zirconia, and titanium reinforcing phases. Because it contains a high percentage of silica, SLS glass is perfect for producing GIC for dental applications (Khiri et al., 2020).

Furthermore, it is a great source of raw material for dental cement glass manufacture. SLS glass has a chemical composition of $SiO_2$ (73.9 wt.%) and CaO (11.2 wt.%), making it an ideal source of silica for glass powder in GIC (Khiri et al., 2020). According to Rahman et al (2019), addition of CaO prevents the glass from becoming water soluble and reduces silica's melting point. As a result, as compared to pure silica, low-melting-point glass can be produced. In Malaysia, however, CS is part of a large volume of waste that is mostly calcium carbonate. Calcium is present in CS in amounts ranging from 95 to 99% by weight. The structural and thermal properties of glass were investigated after it was created using the water quench process (Khiri et al., 2020).

From the previous study of Williams (1987), bioglass is a type of glass that is commonly utilized in biological restoration. The impact of glass composition modifications has been discussed by Williams (1987). Longer working time in the cement and lowered water sensitivity of the set cement are two variations to these fundamental glasses (Williams, 1987). Second, metal powders such as silver, gold, platinum, or palladium can be mixed with the powdered glass (Smith, 1998). Recent study has revealed that the matrix phase contains significant amounts of silica, implying that the glass is completely dissolving rather than undergoing ion-exchange activity on the surface (Rafeek, 2008).

### 2.4.2 Polymer

Polyacrylic acid (PAA) was chosen because of its capacity to complex calcium and generate hydrogen bonds with organic polymers similar to collage (Smith, 1998). PAA is the most common polymer, however acrylic/maleic or acrylic/itaconic copolymers, as well as a 2-methylene butanedioic acid/propenoic acid copolymer, can also be used to make cements. The concentration of acidic polymer is raised when polymeric acids are mixed with glass as a dry powder, without making the liquid too viscous to mix. Polymeric acid in large amounts produces a strong cement, which is required for clinical durability (Nicholson et al., 2020).

Because of its simple structure and low toxicity, PAA was an excellent option. To avoid 'cobwebbing' in the cement mix, the PAA has to have a low molecular weight and a narrow distribution. A chain transfer agent was used to accomplish this. From these perspectives, PAA is a remarkably simple and flexible molecule, which explains its unusual behaviour (Wan Jusoh et al., 2021). The usage of acrylic acid-itaconic acid copolymers can avoid gelation of concentrated PAA solutions on standing due to intra-chain hydrogen bonding. Another solution to this problem was to utilize dry PAA mixed with glass, which just required the addition of water or tartaric acid solution for the cement mix (Smith, 1998).

The presence of PAA in cement, as well as the addition of a specified amount of HA, led in a higher crosslink density in the cement structure, which enhanced GIC mechanical strength (Wan Jusoh et al., 2021). Polymerization shrinkage was a major problem with acrylic materials, as was poor color stability, low modulus, significant thermal expansion, and lack of adherence to the tooth (Williams, 1987). Furthermore,

leakage and bacterial penetration resulted from the combination of shrinkage and lack of adhesion to the cavity walls. Similar acidic cavity primers comprising methacrylic acid and acidic amides were produced by other dental manufacturers (Sidhu & Nicholson, 2016).

To improve acrylic denture base materials, researchers looked on reducing polymerization shrinkage and improving physical qualities by including fillers. When the silicate glass particles were pre-coated with polymer or primed with silane, the materials' characteristics improved (Wan Jusoh et al., 2021). Polyurethane and s-triazine systems were also explored as reactive polymers capable of attaching to collagen. Because of its capacity to complex calcium and generate hydrogen bonds with organic polymers similar to collagen, PAA was chosen. Hence, PAA was especially well-suited because of its simple structure and low toxicity (Smith, 1998).

### 2.4.3 Deionized water

The reaction in the GIC matrix occurs over time in the presence of deionized water, which serves as a setting medium. Water works as a reaction medium, assisting in the maturation and hardening of cement. GIC matrix reaction can be achieved by immersing cements in deionized water for various durations of time as a reaction medium (Wan Jusoh et al., 2021). Using deionized water as the soaking medium, the effects of ageing time on the physical, structural, and mechanical properties of GIC were examined (Khiri et al., 2020). Every 7 days, the deionized water used to maintain the compressive strength specimens was replenished, and the fluoride release was determined using this information. The slow setting of traditional in direct restorative dentistry is a concern (Rafeek, 2008).

A disadvantage of delayed setting, aside from the inconvenience of needing to wait for the restoration to be finished, is that the water content of freshly placed cement can be easily affected by dehydration or saliva water uptake. If an immature repair is not covered with a varnish, dye can enter the surface of a properly set and unprotected glass-ionomer after a few days (Nicholson et al., 2020). Although the loosely bound water reduces the glass-initial ionomer's hardness, it also provides benefits such as shrinkage relief and consistent chemistry across the bulk material, which strengthens the material and encourages fluoride release (Sidhu & Nicholson, 2016).

## 2.5 Mechanical Properties of GIC

The clinical attractiveness of GIC is well known. These cements have properties that make them suitable for use as restorative and adhesive materials, such as adhesion to moist tooth structure and base metals, anticariogenic properties due to fluoride release, thermal compatibility with tooth enamel due to low coefficients of thermal expansion that are similar to those of tooth enamel, biocompatibility, and low cytotoxicity (Rahman et al., 2019). Despite its favourable qualities, GIC's application as a filling and restorative material in dentistry is limited. The mechanical and physical properties of GIC have been demonstrated to be poor, including low fracture strength and hardness, low wear resistance, and poor transparency (Moheet et al., 2018).

Conventional glass-ionomer cements (C-GICs) and resin-modified glass-ionomer cements (R-GICs) are the two types of commercial glass-ionomer cements (RM-GICs). RM-GICs are believed to have better mechanical properties than C-GICs, regardless brand-specific variances. Compressive strength, flexural strength, diametral tensile strength,

fracture toughness, and microhardness are the most common and important mechanical properties used to categorize GIC. Wear rate, fatigue, and creep are all factors to consider when deciding whether to use Knoop or Vickers. (Xie et al., 2000).

Before being used in patients for restorative purposes, conventional cements are tested for compressive strength and must meet a minimum criterion of 100 MPa. In an attempt to compare the materials, several research published compressive strength values for resin-modified glass-ionomers and flexural strength values for regular glass-ionomers. Despite what different research assert, reported values vary greatly, making it impossible to make any accurate conclusions (Rodrigues et al., 2015).

According to a study, the standard glass-ionomer Fuji IX (GC, Tokyo, Japan) has a compressive strength of 83.6 MPa after 24 hours and 350.87 MPa after 48 hours in its hand-mixed form (Rodrigues et al., 2015). Compressive strength levels of conventional glass-ionomers have also been reported to be low. Vitremer (3M-ESPE, Seefeld, Germany), for example, had a compressive strength of 169.50 MPa, while the material Ionofil Molar (VOCO, Cuxhaven, Germany) had a compressive strength of 78.78 MPa (Nicholson et al., 2020). The findings of this study reveal that there are some important general correlations between commercial GIC compositions, microstructures, and mechanical properties (Xie et al., 2000).

Many efforts have been made to modify GIC in order to improve its physical and mechanical qualities. Incorporating hydroxyapatite into the GIC composition is one option. When HA is introduced to GIC, the acid polymer's $H^+$ attacks the ceramic particles during the formation and cross-linking of the polysalt bridge, resulting in the production of an intermediate layer (Mollazadeh et al., 2013). The intermediate layer is extremely acid

resistant and difficult to break. As a result, adding HA to GIC improves the mechanical strength of the final GIC. Furthermore, several research have shown that increasing the crosslink density of the cement structure by adding a certain amount of HA, as well as the role of PAA in cement, helped to raise the mechanical strength of the GIC (Wan Jusoh et al., 2021).

### 2.5.1 Heat Treatment

Heat treatment effects on the glass component for GICs have been investigated in terms of microstructure, crystallization, and phase transition. Heat treatment resulted in an increase of particle size and phase changes. The glass was deactivated with heat treatment, giving the surgeon more time to handle the prosthetic (Gu & Fu, 2004). In terms of microstructure, crystallzsation, and phase transition, the impacts of heat treatment on the glass component for GICs have been examined. Amorphous glass can transform into more thermodynamically stable crystalline phases when heated to specific temperatures (Stanton & Hill, 2005).

Glass powder form and phase composition, as well as temperature and activation energy, were studied in relation to phase changes after heat treatment. The particle size of the powders appears to grow as the heat treatment temperature rises. Because of particle agglomeration, coalescence, and growth at high temperatures, particle size rises after heat treatment. Glass particles have a disordered and amorphous structure before they are heated (Jusoh et al., 2019).

The presence of strontium fluoride phosphate ($Sr_5(PO_4)_3F$) and mullite ($Al_6Si_2O_{13}$) is revealed by XRD after heat treatment (Stanton & Hill, 2005). Mullite, coupled with strontium fluoride phosphate, forms a second phase. When heated, amorphous glass

powders for glass ionomer cements rapidly convert into crystalline phases, and this amorphous–crystalline transition is most likely due to an amorphous–crystalline transition associated to surface crystallization (Khiri et al., 2020). Because of diverse particle agglomeration, coalescence, and growth at high temperatures, the particle size of glass powders increases as the heat treatment temperature rises (Gu & Fu, 2004).

Heat treatment had little effect on the conventional GIC employed in Rafeek's research, but it had a significant effect on the resin modified GIC, enhancing compressive strength and modulus while lowering stress relaxation properties and fluoride release. The influence of humidity, temperature, and heat treatment on the bond strength, setting reaction, and strength of glass ionomer cements has been studied in other studies (Smith, 1990). The use of radiant heat on a conventional GIC was subsequently explored, and it was discovered that at temperatures above 37 °C, the compressive strength of restorative GIC can be increased. A higher degree of conversion is expected if heat is provided during the curing process, which could reduce the amount of material that is leachable (Rafeek, 2008). Heat or ultrasonic treatment can also improve mechanical characteristics significantly.

### 2.5.2 Incorporation of Hydroxyapatite into GIC

Hydroxyapatite (HA) is a well-known inorganic compound of the apatite group (a group of mineral phosphates) with a composition similar to natural bone material. $Ca_{10}(PO_4)_6(OH)_2$ is the chemical formula for HA, which differs from other apatite compounds because it contains the hydroxyl end-member of the apatite group (Nicholson

et al., 2020). Because of its osteoconductive and bioactive properties, HA is useful in orthopaedics and dentistry. The addition of HA to GIC resulted in better compressive strength than GIC without HA, according to compression strength testing. This is due to a crystal phase in the structure of the glass ionomer. Metal ions, such as $Ca^{2+}$, are displaced by the addition of HA, resulting in enhanced ion participation in the acid-base reaction (Wan Jusoh et al., 2021).

During the polysalt bridge formation and cross-linking process, the acid polymer's $H^{+}$ binds to the ceramic particles, forming an intermediate layer. As a result, incorporating HA into GIC improves the final GIC's mechanical strength (Wan Jusoh et al., 2021). Figure 2.1 shows a schematic picture of the setting reaction of HA added GIC.

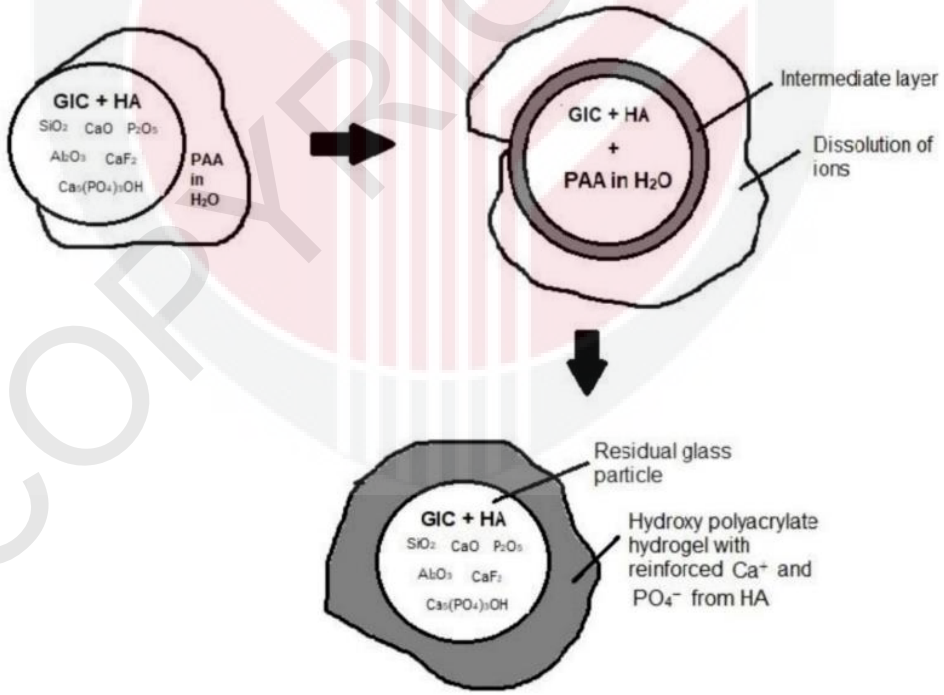



**Figure 2.1** Schematic diagram of setting reaction of HA-added GIC (Wan Jusoh et al., 2021)

Several investigations on polycarboxylic acid adsorption on HA have been conducted since then, although the exact mode of binding remains unknown. Adsorption of polyalkenoic acids to HA was shown to be varied in respect to structure in previous research (Moheet et al., 2018). As a result, adsorption does not appear to be linked to adhesion properties. The concept of incorporating polymerization and polyelectrolyte salt formation mechanisms within one molecule or a combination of molecules has resulted in a wide range of materials, ranging from traditional acid-base GIC to modified polymer-ceramic (glass) composites with little polyelectrolyte character (Smith, 1998).

### 2.5.3 Ageing Time

The GIC samples were immersed in distilled water for 1, 7, 14, 21, and 28 days, depending on the ageing time. At various ageing times, the physical, structural, and mechanical properties of GIC samples were examined. Allowing GIC to mature in liquid will improve its mechanical properties. The cement was carefully removed from the moulds after one hour and stored in deionized water in an incubator at 37°C. After immersion, the ageing time of GIC was measured at 1, 7, 14, 21, and 28 days (Khiri et al., 2020).

To see if there was a significant difference in density and compressive strength between different ageing times for each cement sample, Turkey-Kramer post-hoc analysis was used. According to density results, compressive strength results exhibited significantly varying outcomes when compared to different ageing durations. As a result of the increased

ageing time, the compressive strength value increased significantly (Wan Jusoh et al., 2021).

## 2.6 Physical and Structural Properties of GIC and HA-added GIC

The physical properties of both GIC and HA-added GIC samples were investigated using density measurement in recent research. With the addition of HA powder, GIC density increases. Because HA has a higher density than ASF glass ceramics samples, this is the situation. The polymer has an impact on the properties of the resulting glass-ionomer cement (Thoo et al., 2013). Higher molecular weight polymers improve set cement strength, but their solutions have high viscosities, making mixing difficult. As a result, molecular weights are selected to counteract these opposing effects. The compressive strength of cements made from acrylic acid homopolymers improves after the first 4-6 weeks (Abo-Mosallam et al., 2016). The powder:liquid ratio, polyacid concentration, glass powder particle size, and specimen age all influence the physical properties of glass ionomer cements (Wan Jusoh et al., 2021).

As a result, generalisations concerning the qualities of these materials must be used with caution. It is also likely that glass-ionomers' success stems from their ability to work effectively even when not properly mixed or allowed to grow under optimal circumstances (Moheet et al., 2018). Minimum values for several physical properties are established in the current ISO standard for glass-ionomers. These values, as shown in Table 2.1, are the minimum requirement that a material must meet in order to be approved for

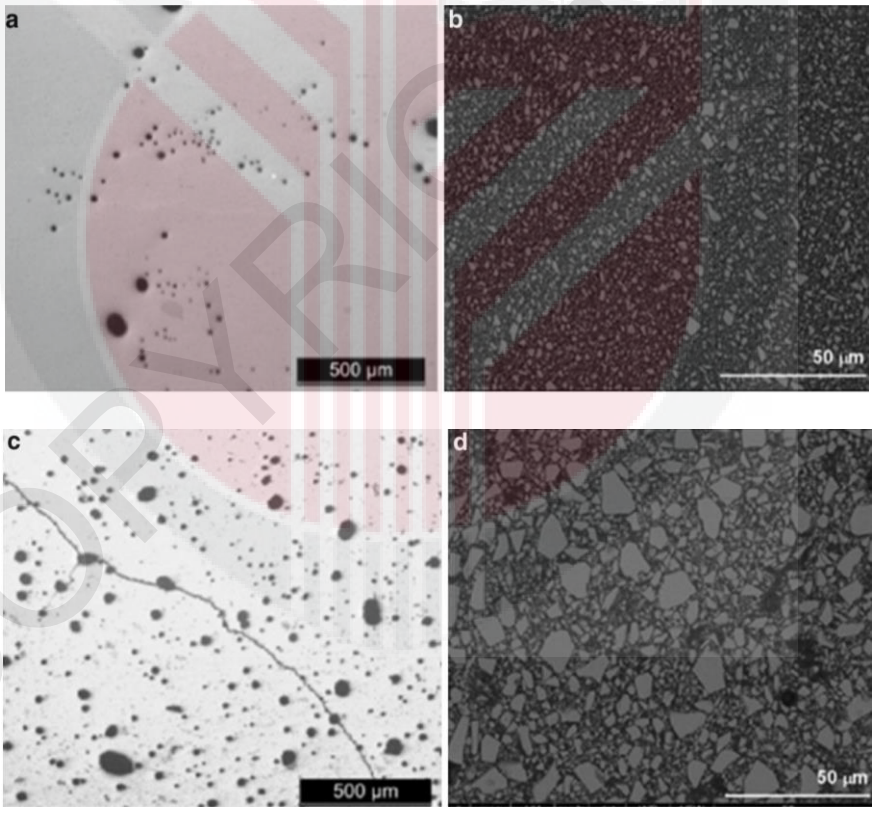
commercialization, rather than typical of products that have been proven effective in clinical studies. Glass-ionomers can also take up ions (Sidhu & Nicholson, 2016).

Natural saliva's cements absorb calcium and phosphate ions, making the surface more harder. Glass-ionomer cements form a substance deep within the fissure that includes more calcium and phosphate than the original tooth structure and is much more resistant to cutting with a dental drill when used as fissure sealants. The residual material is said to resemble enamel because of the better drilling resistance and the change in appearance (Sidhu & Nicholson, 2016).

**Table 2.1** ISO requirements for clinical grade glass-ionomer cements (Sidhu & Nicholson, 2016)

| **Property** | **Luting Cement** | **Restorative Cement** |
|---|---|---|
| Setting time/min | 2.5 - 8 | 2 – 6 |
| Compressive strength/MPa | 70 (minimum) | 100 (minimum) |
| Acid erosion (maximum)/ mm $h^{-1}$ | - | 0.05 |
| Opacity, $C_{0.70}$ | - | 0.35 – 0.90 |
| Acid-soluble As/mg $kg^{-1}$ | 2 | 2 |
| Acid-soluble Pb/mg $kg^{-1}$ | 100 | 100 |

For microstructural analyses, the images of the materials utilized in this study obtained by optical microscope are presented in Figure 2.2. In compared to glass-ionomer materials, the nano-hybrid resin composite demonstrated a decreased number of pores (black circle points) (Figure 2.2a) (Figure 2.2c, e). Cracks were discovered around the fillers, as well as between the pores in glass ionomer. Back scattered electron micrographs of the materials surface are also visible in FEG-SEM micrographs (Figure 2.2 b,d and f). The filler size in resin composite was smaller (Figure 2.2b) than in resin-modified (Figure 2.2d) or conventional ionomer (Figure 2.2f) (Rodrigues et al., 2015).



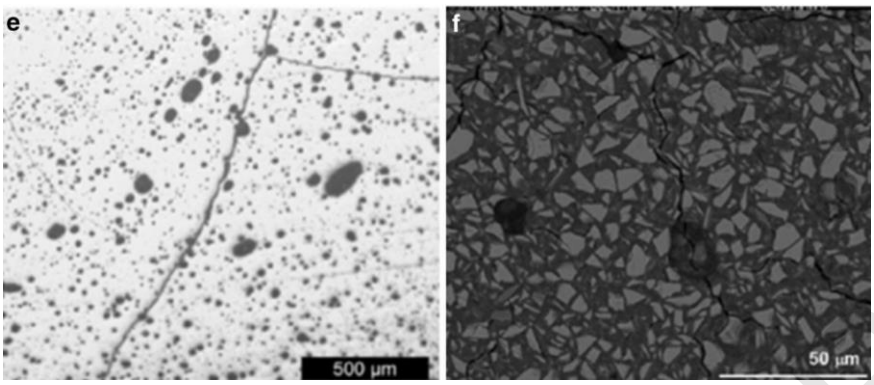



**Figure 2.2** Images of a resin composite, **a** resin-modified glass ionomer, and a regular glass ionomer taken with an optical microscope (pores appear as *dark circular points*). **b** resin composite, **d** resin-modified glass ionomer, and **f** conventional glass ionomer FEG-SEM images (images obtained at 92000 magnification by back scattered electron mode at 15 kV) (Rodrigues et al., 2015).

GIC formed with ASF glass ceramics as the base silicate powder improved in physical, mechanical, and structural properties, revealing an increase in density and compressive strength tests, as well as the development of the Fluorohydroxyapatite (FHA) crystal phase from structural research, where FHA is fluorine incorporation into the HA structure (Klos et al., 2020). Furthermore, it has been discovered that increasing the ageing time increases the GIC's properties. In a nutshell, the enhanced physical, structural, and mechanical properties of the HA-added GIC support its use in biomedical applications, especially tooth restoration (Wan Jusoh et al., 2021).

# CHAPTER 3

# RESEARCH METHODOLOGY

## 3.1 Introduction

This chapter explains on how to make ASF based glass ceramics out of CS and SLS glass. To fabricate GIC, ASF based glass ceramics were used in this study. The methods that have been used to prepare glass ceramic samples are conventional melt water quenching technique and controlled crystallization process with sintering temperatures of room temperature, 600 °C, 700 °C and 900 °C. In this research, heating process and solid state sintering process were used to form sintered material. Density measurement, XRD, FTIR and FESEM were used to characterize the sample and to observe density and microstructure of the sample.

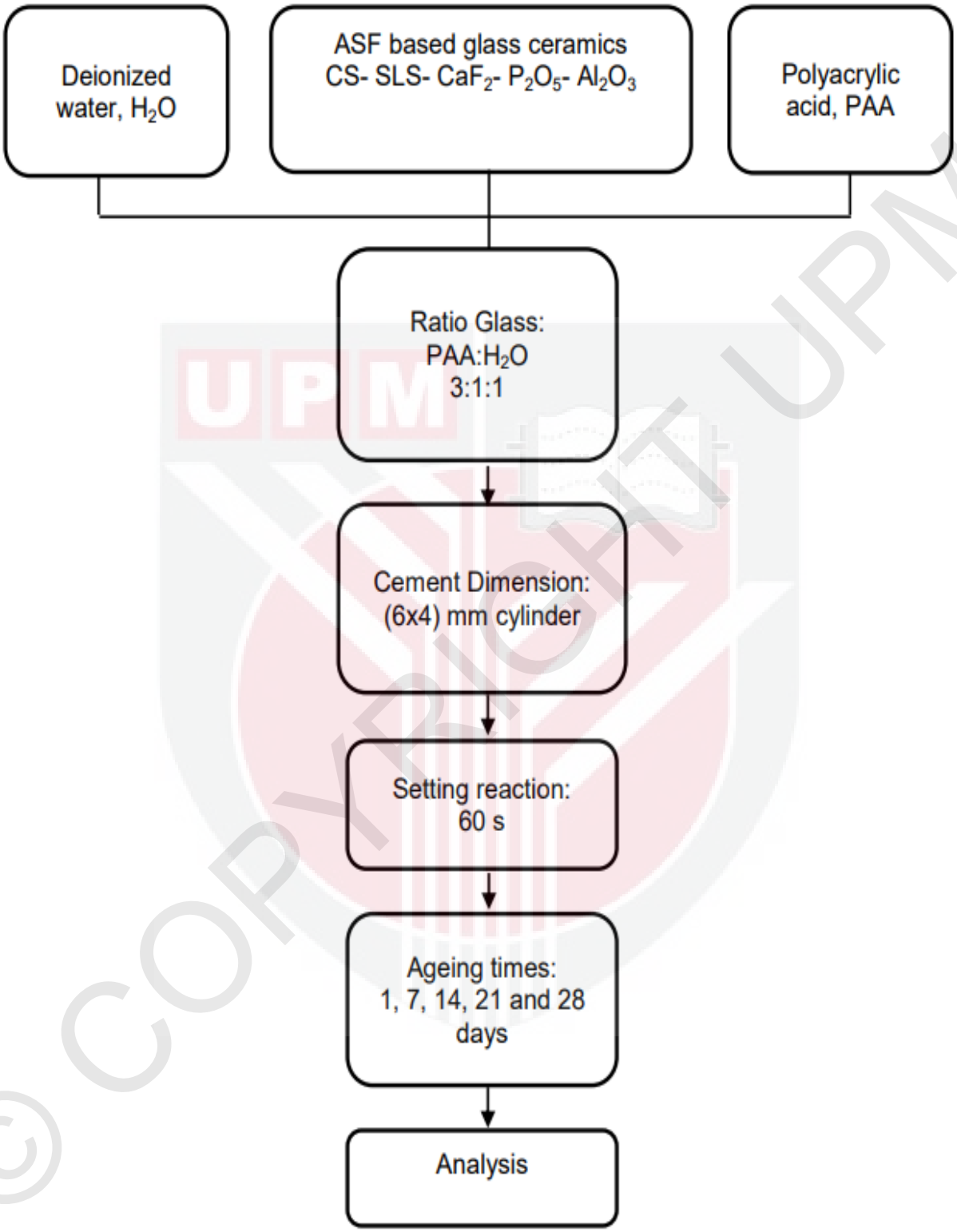



**Figure 3.1** Overview of GIC sample preparation

## 3.2 Sample Preparation

The raw materials for GIC samples were ASF glass powder, Polyacrylic acid, PAA, and deionized water, which were prepared first. Following a 3:1:1 ratio with deionized water and PAA, GIC samples can be prepared.

## 3.3 Preparation of Raw Materials

There are two types of materials used in the preparation of samples for ASF-based glass ceramics which are waste and commercial. SLS glass and CS wastes are utilized in the synthesis of glass ceramics. By substituting silica and calcium in the glass ceramic composition, both residues become the precursor element. Glass frits of ASF glass were prepared before mixing with PAA to prepare the raw ingredients. The composition of ASF glass powder was originally determined using CS powder, SLS powder, $CaF_2$ powder, $P_2O_5$ powder, and $Al_2O_3$ powder, using the formula $15CS{\cdot}25SLS{\cdot}20CaF_2{\cdot}20P_2O_5{\cdot}20Al_2O_3$ as shown in Table 3.1.

**Table 3.1** The ratio of weight percentage for ASF based glass ceramics sample.

| | Chemical Composition | | | | |
|---|---|---|---|---|---|
| **Sample** | **SLS** | **CS** | **$CaF_2$** | **$P_2O_5$** | **$Al_2O_3$** |
| **ASF** | 25 | 15 | 20 | 20 | 20 |

This mixture was milled and then melted in an electrical furnace at 1500 °C for 4 hours, as shown in Figure 3.2(a). Glass frits were formed by passing the molten sample glass through the water quenching process, which generates thermal shock. The glass frits formed during the quenching process were left to dry at room temperature before being crushed with a plunger as shown in Figure 3.2(b). The plunged glass frits were grinded using mortar and pestle as shown in Figure 3.2(c). Then, the glass was sieved with siever of 45 μm of particle size to obtain a homogenous and fine small glass powder.

**(a)** Electrical Furnace **(b)** Plunger

**(c)** Pestle and Mortar

**Figure 3.2** Preparation of raw materials using (a) electrical furnace, (b) plunger and (c) pestle and mortar.

## 3.4 Sintering of glass powder

The sintering process was performed to see certain changes in physical and structural as the sintering process was applied to the glass powder. The process of powdering, where grinding and sieving are done repeatedly to make sure the glass powder are in 45 μm of particle size to obtain a homogenous and fine small glass powder. Glass powder samples were sintered at four different temperatures which are 30, 600, 700 and 900 °C.

## 3.5 Preparation of GIC samples

To make GIC cement, three major components were used which are an ASF-based glass ceramics powder, PAA, and $H_2O$. The ratio of glass: PAA: $H_2O$, which is 3:1:1, was used to make cement from these three ingredients. An acid-base reaction technique was used to create a GIC sample, with the ASF glass powder being alkaline and the PAA being an acidic solution. GIC samples were made with the polymer PAA, which has a molecular weight of 30,000. For about 60 seconds, the mixture was vigorously stirred with a spatula until it was uniform. The setting reaction of the cement takes place at this stage.

### 3.5.1 Moulding and Pelleting

The GIC cement was mixed by hand using the mixed-method approach, as follows: Using a spatula, mix glass:PAA:$H_2O$ for around 60 seconds. Within 60 seconds of finishing the mixing operation, the cement was poured into a stainless steel mould (height 6 mm, diameter 4 mm) as indicated in Figure 3.3. The cement was pressed between two metal plates and heated for roughly 1 hour at 37 °C.

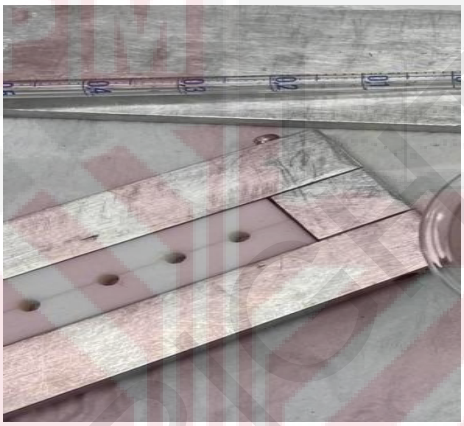


**Figure 3.3** Steel Mould

### 3.5.2 Ageing Times

After 1 hour, the GIC cement was gently removed from the mould and stored in deionized water. The GIC was soaked for 1, 7, 14, 21, and 28 days during the ageing process. For the ageing times, the GIC samples were immersed in deionized water to mimic the humid state of the teeth. The mechanical characteristics of GIC are thought to be improved by the ageing process in liquids (Khiri et al., 2020).

## 3.6 Characterization

To determine the properties of raw samples before GIC preparation, ASF based glass ceramics were characterized. GIC samples were characterized using different measurement such as by density measurement, XRD, FTIR and FESEM.

### 3.6.1 Density Measurement

The density of the glass is used to characterize its physical properties in terms of mass and volume. The SI unit kg/m$^3$ is used to represent density as mass per volume. The Archimedes principle is used to calculate the density of GIC samples in pellet form with a cylindrical dimension of (height 6 mm, diameter 4 mm). According to the Archimedes principle, the apparent weight of an immersed object will be less than the real weight due to the amount of fluid displaced. Using an electronic balance with a precision of ±0.001 g, the GIC inform of pellets was weighted in air and water, $W_{air}$ and $W_{water}$ respectively (Khiri et al., 2020). The density was calculated using Equation 3.1:

$$\rho = \frac{W_{air}}{W_{water}} \times (\rho) \tag{3.1}$$

Where, $W_{air}$ is the weight sample in air, $W_{water}$ is the weight sample in distilled water and $\rho_w$ is the density of distilled water. Density of distilled water is 1.000 g/cm$^3$.

### 3.6.2 X-ray Diffraction Spectroscopy (XRD)

The phase of the GIC sample in homogenous powder form was investigated using XRD analysis. The GIC phases were investigated in order to discover whether the structure is amorphous or crystalline. In addition to phase identification, XRD also provides information about the unit cell's dimension. Diffraction occurs from plane, and angle 2θ is the diffraction angle with relation to incident light. The XRD measurement was done from 20° to 80° for this study. An X-ray Phillips (Model PW 1830) with CuK$\alpha$ radiation = 1.5418 at 40 kV and 30 mA of input current was used to determine the structure of the sample. Using the X'Pert Highscore software, the findings were then extracted. As shown in Figure 3.6, the interactions for XRD analysis have met Bragg's law conditions (Khiri et al., 2020).

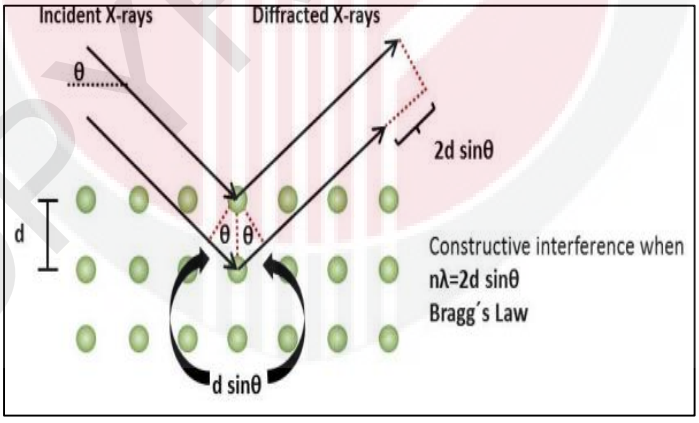



**Figure 3.4** Schematic diagram of the Bragg equation (Khiri et al., 2020)

### 3.6.3 Fourier transform infrared spectroscopy (FTIR)

By absorbing infrared radiation in vibrational mode, the FTIR was utilized to determine the functional group in a material. The FTIR technique is a non-destructive method for determining the composition and structure of materials. The absorbed infrared energy stimulates a molecule to a higher vibrational state when it is bombarded with infrared radiation. The wavelength of light absorbed by a specific molecule is determined by the energy difference between the state of vibration at rest and stimulation. The wavelengths absorbed by the sample determine the molecular structural properties. The UATR-FTIR (Universal Attenuated Total Internal Reflection Fourier Transform Infrared) spectra detected the homogenous sample powder with 45 μm particle size.

### 3.6.4 Field emission scanning electron microscopy (FESEM)

At magnifications ranging from 5000 to 100 000, FESEM represents topography and elemental information with nearly infinite field depth. The FESEM can provide a range of magnified specimen images and offers digital imaging with ultra-high resolution. There are two vacuum operating modes on this machine which are high vacuum and low vacuum. To detect the morphology of the sample structure, the 45 μm of particle size powder sample was coated with silver (Ag). The goal of sample coating during FESEM is to improve image quality by forming a conductive metal layer on the sample that prevents charging. Microstructural analysis was performed using a FESEM on CFAS glass and GIC samples aged for 7–28 days (Khiri et al., 2020).

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Introduction

In this chapter, the results of the physical and structural properties analysis of ASF based glass ceramics and GIC samples are extensively discussed. GIC was investigated when it was especially combined with ASF-based glass ceramics. The density measurement, XRD, FTIR, and FESEM were used to characterize the phase formation, morphology, and enhanced mechanical characteristics of GIC.

## 4.2 Physical properties of GIC

The physical properties of GIC were investigated using density measurements. In this part, we focused at the density of GIC samples at various sintering temperatures and ageing times.

### 4.2.1 Density Measurement

Table 4.1 shows the density result for four samples of GIC with different temperatures according to ageing times 1, 7, 14, 21 and 28 days. The densities of the samples were determined according to Archimedes' method.

**Table 4.1:** Density of GIC at various sintering temperatures and different ageing times.

| | Density at | Different | Temperature | (g/cm$^3$) | |
|---|---|---|---|---|---|
| **Temperature °C / Ageing Time (days)** | **1 day** | **7 days** | **14 days** | **21 days** | **28 days** |
| **Room Temperature** | 1.773 | 1.756 | 1.698 | 1.799 | 1.693 |
| **600** | 1.813 | 1.703 | 1.785 | 1.844 | 1.7583 |
| **700** | 1.650 | 1.770 | 1.824 | 1.816 | 1.793 |
| **900** | 1.585 | 1.753 | 1.729 | 1.668 | 1.683 |

From Table 4.1, it shows the density of GIC samples at various sintering temperatures and different ageing times. Meanwhile, Figure 4.1 depicts the overall trend for GIC samples incorporating various sintering temperatures at various ageing times. From Figure 4.1, the densities of GIC samples for 1 day of ageing times kept increasing from room temperatures until 600 °C, then densities decrease at the temperature of 700 °C and 900 °C. For 1 day, the densities of the samples were in the range of 1.5 $gcm^{-3}$ until 1.8 $gcm^{-3}$.

Next, for 7 days of ageing times, the relationship of density with sintering temperature shows that the density pattern decrease throughout the sintering temperatures to 600 °C. Then, the density increases at sintering temperature of 700 °C and kept decreasing at 900 °C. The samples had density of around 1.703 $gcm^{-3}$ to 1.770 $gcm^{-3}$.

The densities of GIC samples shows increasing trend starting from room temperatures to 700 °C for 14 days of ageing times and decreasing at 900 °C which

indicates the relationship of density with sintering temperature The densities of the samples were in the range of 1.6 $gcm^{-3}$ until 1.8 $gcm^{-3}$.

Moreover, the samples had density of around 1.6 $gcm^{-3}$ to 1.8 $gcm^{-3}$ for ageing times of 21 days. From Figure 4.1, it shows the same pattern as ageing times of 1 day, where the densities increasing from room temperature until 600 °C. Then, the density dropped at sintering temperatures of 700 °C and 900 °C.

For ageing times of 28 days, there were slightly changes for the densities of GIC samples at room temperature and 600 °C. The relationship of density with sintering temperature shows that the density pattern increases throughout the sintering temperatures to 700 °C. Then, the density decreases at sintering temperature of 900 °C. It can observe that the trend for density is decreasing from 1 day to 28 days of ageing time at 900 °C.

Meanwhile, the relationship of density with the ageing times of GIC shows changes for all sintering temperatures. At room temperature, the density increases throughout 1 day to 14 days. Then, the density shows an increment pattern at 21 days and dropped again at ageing times of 28 days. Next, at sintering temperatures of 600 °C, the density decreases from 1 day to 7 days. At 14 to 21 days, the density started to increase and continue to decrease at 28 days. The relationship of density with the ageing times at 700 °C shows an increment pattern throughout 1 to 14 days. However, at 21 to 28 days, it shows a decrement pattern of density. At the highest sintering temperatures which is at 900 °C, the density increases from 1 day to 7 days. At 14 to 21 days, the density started to increase and continue to decrease at 28 days.

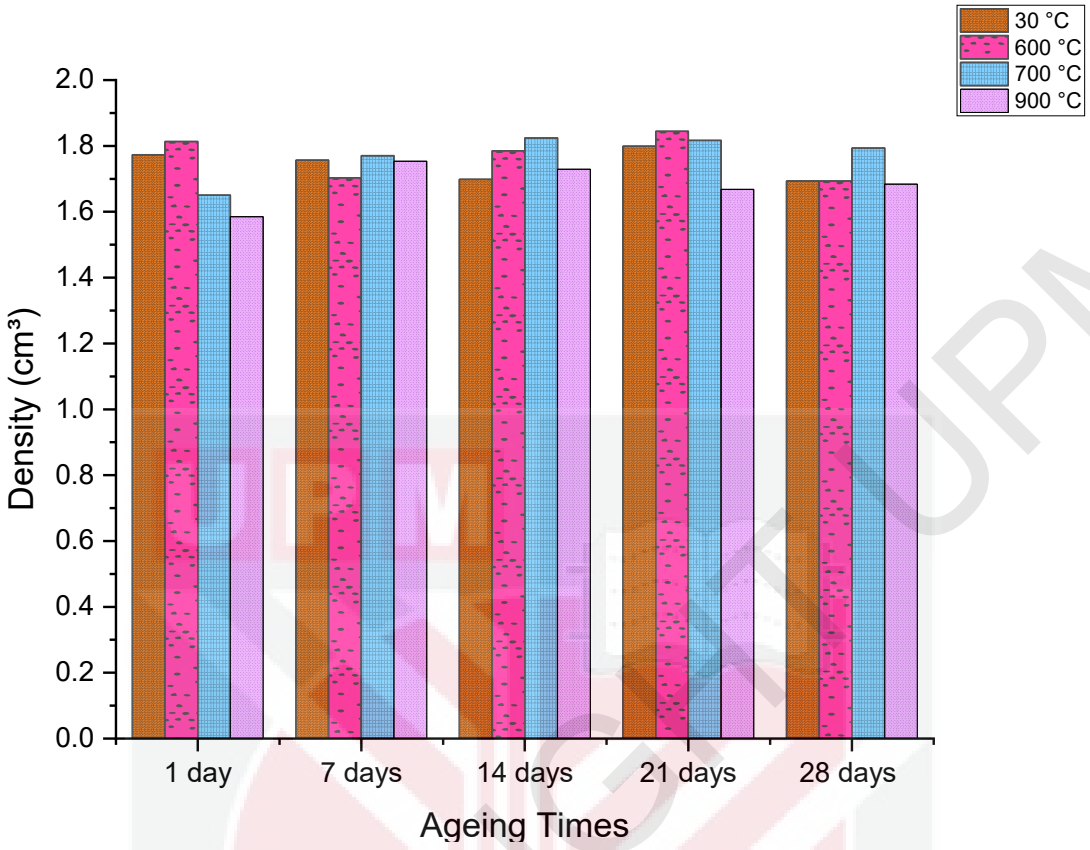



**Figure 4.1** Density of GIC at various sintering temperatures and different ageing times

Rise in density may be owing to particle rearrangement caused by increasing viscosity, and sintering happens during the crystallization process via viscous flow. Hence, samples will harden as a result of this outcome (de Sousa et al., 2008). At 700 °C to 900 °C, the density shows a decrement pattern because of the phase changes in the GIC as discussed in subtopic 2.5.1. During the sintering of glass at various sintering temperatures, some potential processes, including as oxidation-reduction and phase transition, have been observed in prior research (Zarifah et al., 2015). This reaction can result in a decrease in density due to an increase of close pores. The maturation and hardening process of GIC

cement may be one of the possible causes of increased densities over time. This reaction will increase the physical strength of the GIC sample (Khiri et al., 2020).

## 4.3 Structural properties of GIC

Using XRD, FTIR, and FESEM analysis, the structural characteristics of GIC were determined.

### 4.3.1 XRD Analysis of GIC

The crystal phase of the sample is determined using XRD analysis**.** The XRD patterns of GIC at room temperature, 600 °C, 700 °C, and 900 °C with ageing times of 1, 7, 14, 21, and 28 days are shown in Figures 4.2, 4.3, 4.4 and 4.5 and summarized in Table 4.3.

Figure 4.2 shows the XRD pattern of GIC at room temperatures with ageing times from 1 until 28 days. The highest intensity peak was detected in the GIC samples at about 31.9° with intensities of 3320, 2920, 4200 and 4500 a.u. From the XRD analysis, it shows that the pattern of intensity is decreasing from 1 to 14 days and the value of intensity increases at 21 to 28 days. The highest intensity phase of diffraction peak for 1, 7, 14, 21 and 28 days are 3320 a.u, 2720 a.u, 2040 a.u, 2070 a.u and 2640 a.u respectively. Starting from room temperature, the main phase existed for every ageing times was Fluorapatite ($Ca_5(PO_4)_3F$) phase (ICSD code: 98-001-7206).

Next, XRD pattern of GIC at 600 °C with ageing times of 1, 7, 14, 21 and 28 days is shown in Figure 4.3. From XRD analysis, it can be seen that the pattern of the highest peaks for different ageing times is increasing from 1 to 21 days and the intensity decrease at 28 days. The highest intensity phase of diffraction peak for 1, 7, 14, 21 and 28 days are 3320 a.u, 2720 a.u, 2040 a.u, 2070 a.u and 2640 a.u respectively. Fluorapatite is the main phase existed at 600 °C.

At 700 °C, the highest intensity phase of diffraction peak was detected in the GIC samples at 28 days of ageing times which is 4200 a.u. At 1 day of ageing time, the value of intensity is 3300 a.u and decrease to 2490 a.u at 7 days. The intensity kept increasing at 14 and 21 days which are 2730 a.u and 2920 a.u respectively. The main phase existed at 700 °C is Fluorapatite.

XRD pattern of GIC at 900 °C with ageing times of 1, 7, 14, 21 and 28 days is shown in Figure 4.5. For 1 and 7 days, the phase existed are Fluorapatite and Anorthite. Meanwhile, Fluorapatite, Anorthite ($Ca(Al_2Si_2O_8)$) and Mullite ($Al_5SiO_{9.5}$) are the phases existed at 14, 21 and 28 days. From XRD analysis, it can be seen that the pattern of the highest peaks for different ageing times is decreasing from 1 to 7 days. Then, the value of intensity kept increasing at 14 days and dropped back at 21 days. However, it shows an increment pattern of intensity at 28 days. The highest intensity phase of diffraction peak for 1, 7, 14, 21 and 28 days at 900 °C are 4500 a.u, 3600 a.u, 4200 a.u, 2200 a.u and 4200 a.u respectively.

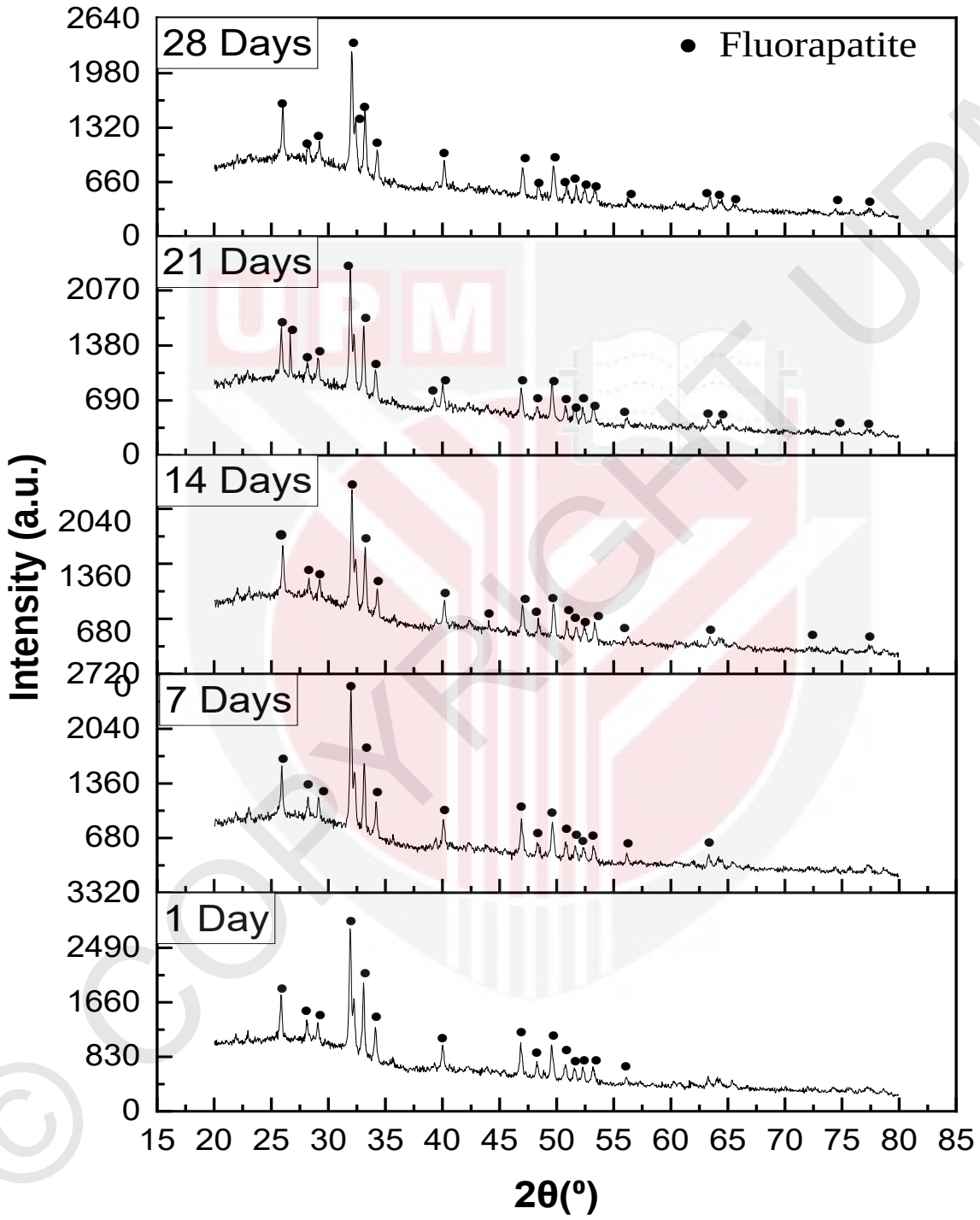



**Figure 4.2** XRD pattern of GIC at room temperatures with ageing times 1, 7, 14, 21 and 28 days.

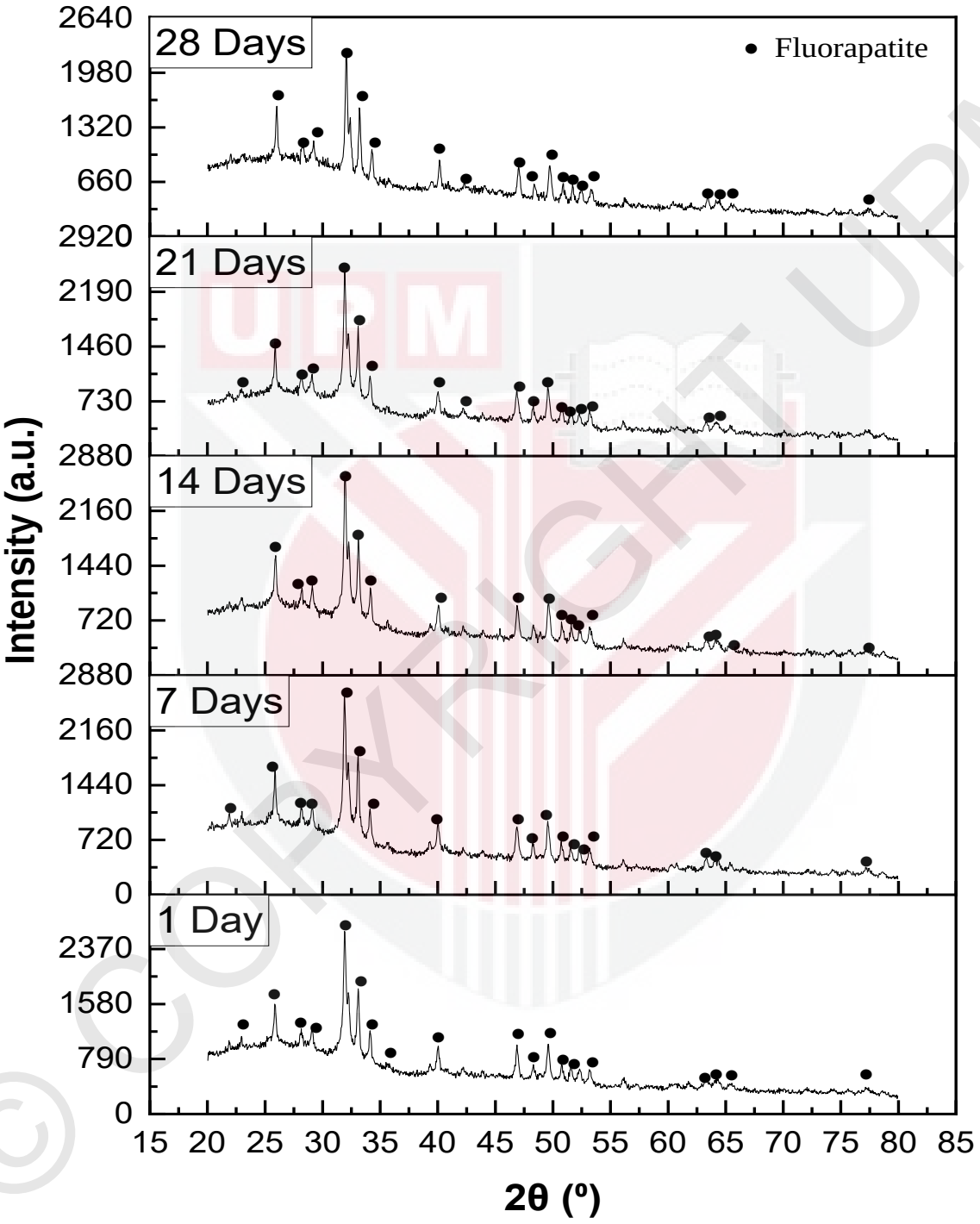



**Figure 4.3** XRD pattern of GIC at 600 °C with ageing times 1, 7, 14, 21 and 28 days.

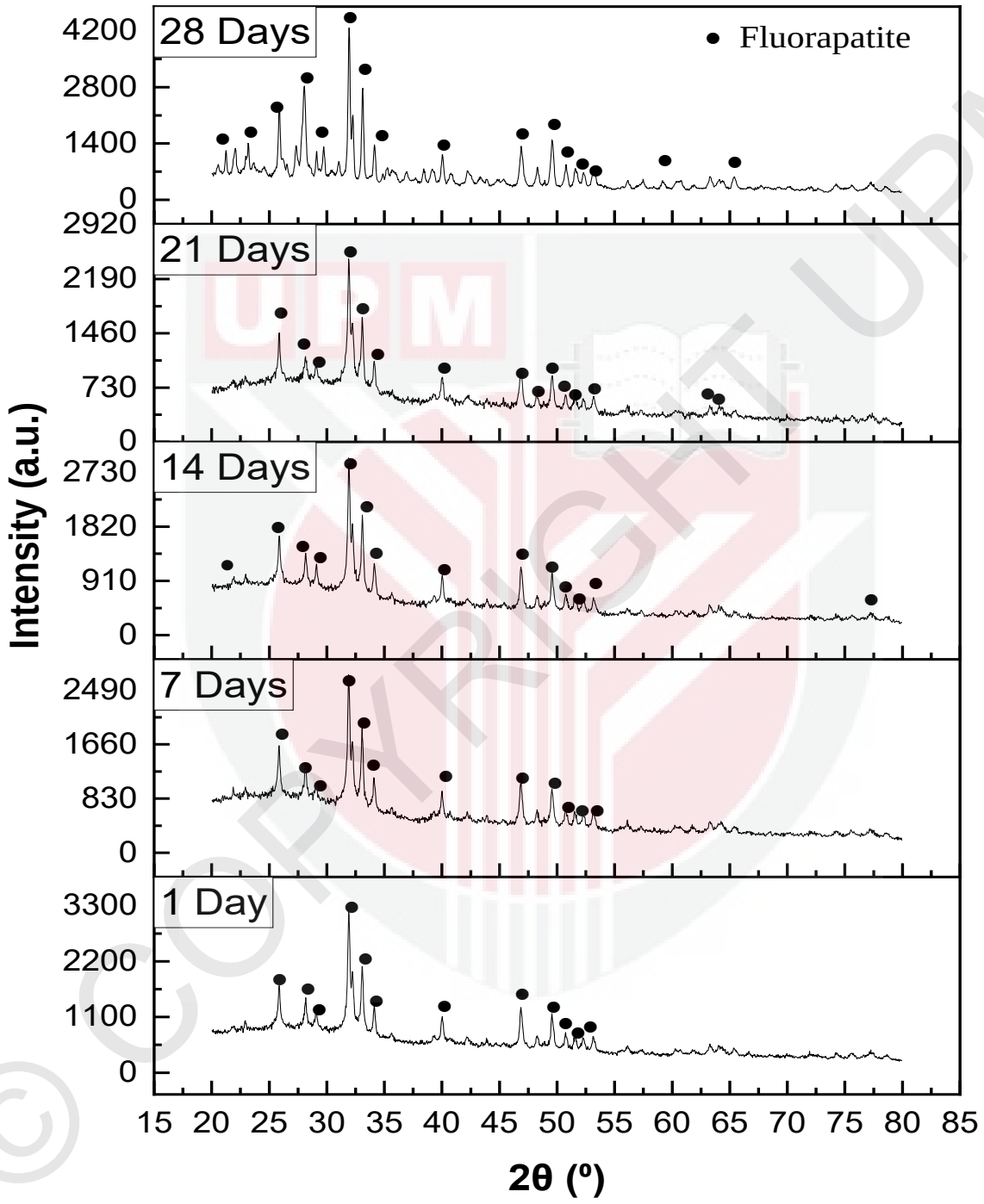



**Figure 4.4** XRD pattern of GIC at 700 °C with ageing times 1, 7, 14, 21 and 28 days.

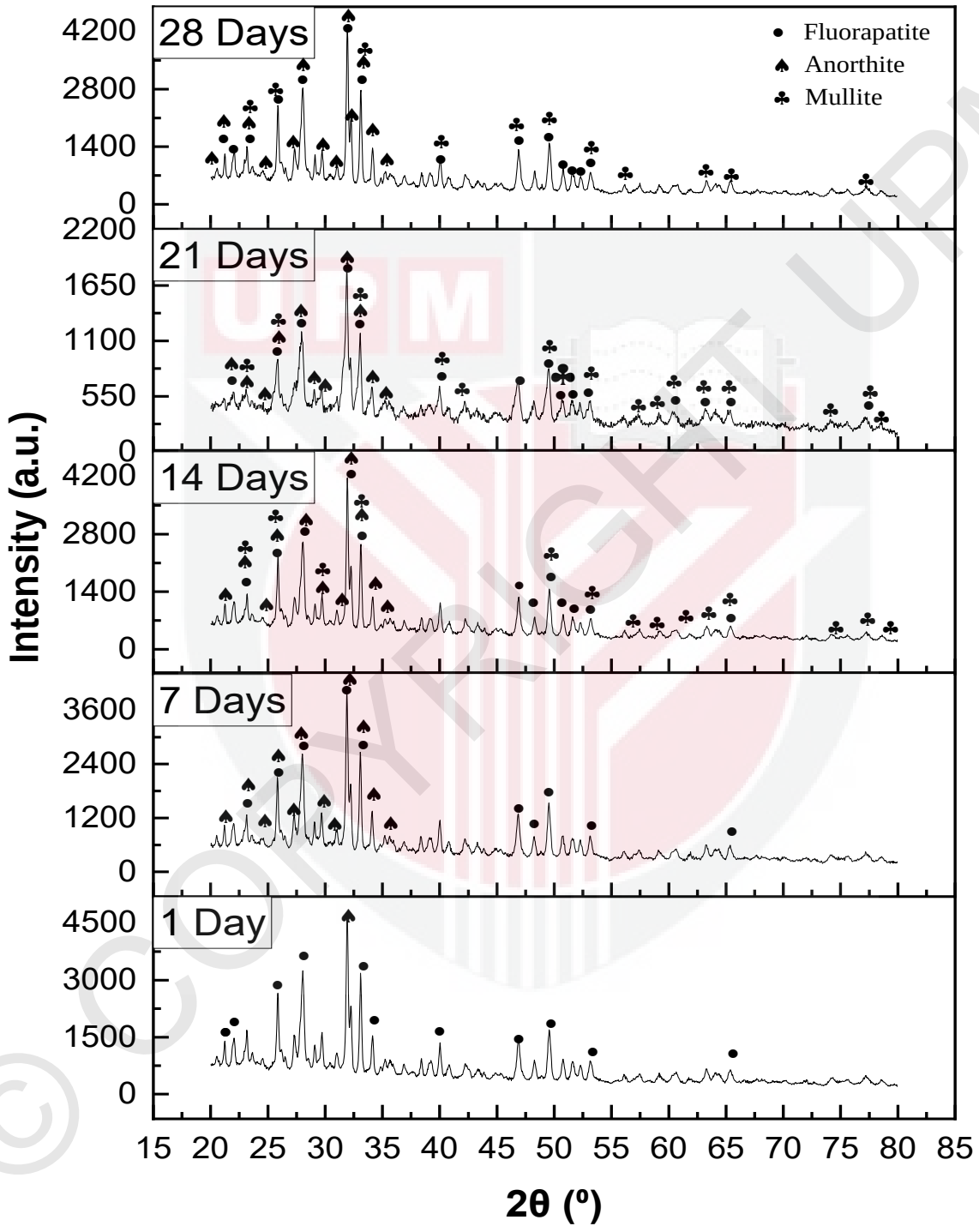



**Figure 4.5** XRD pattern of GIC at 900 °C with ageing times 1, 7, 14, 21 and 28 days.

Due to the ASF glass powder's unstable chemical composition, the fluorapatite phase was found in the GIC sample (Jusoh et al., 2019). Furthermore, before the sintering process, it becomes the primary phase in the glass, where it encourages bone development, lowers solubility, and improves mechanical strength. Generally, fluorapatite crystals are well-known in dentistry because of their ability to remain stable in an acidic environment (Stanton & Hill, 2005).

From XRD analysis, a phase transition occurs from fluorapatite to anorthite and mullite can be observed at high sintering temperature which is 900 °C. Glass' mechanical and thermal properties are assumed to be improved as a result of the formation of these phases, making it more suitable for dental usage. The optimum nucleation rate of the apatite phase was reached without the formation of the mullite phase at 600 °C, which was chosen as the best temperature for nucleation. Meanwhile, the nucleation temperature of glass with the same composition is around 783 °C (Mollazadeh et al., 2013).

The formation of additional phases was slower during 1 day of ageing, with the anorthite and mullite phases starting to form at 900 °C. Other ageing times of 1, 7, 14, 21, and 28 days are not the same. Other ageing times show a similar apatite development pattern, with the fluorapatite phase beginning to form at low temperatures, such as room temperature, and continuing until 700 °C. Then, at 900 °C, anorthite and mullite are formed.

**Table 4.2** Crystalline phase of GIC at various sintering temperatures and different ageing times.

| Temperature (°C) / Ageing time (days) | Crystalline phase | | | | |
|---|---|---|---|---|---|
| | 1 day | 7 days | 14 days | 21 days | 28 days |
| **Room Temperature** | Fluorapatite | Fluorapatite | Fluorapatite | Fluorapatite | Fluorapatite |
| **600** | Fluorapatite | Fluorapatite | Fluorapatite | Fluorapatite | Fluorapatite |
| **700** | Fluorapatite | Fluorapatite | Fluorapatite | Fluorapatite | Fluorapatite. |
| **900** | Fluorapatite, Anorthite | Fluorapatite, Anorthite | Fluorapatite, Mullite, Anorthite | Fluorapatite, Mullite, Anorthite | Fluorapatite, Mullite, Anorthite |

### 4.3.2 FTIR Analysis of GIC

Figure 4.6 shows FTIR patterns of GIC for 7, 14 and 21 and 28 days of ageing time while Table 4.4 depicted FTIR spectral bands assigned to the vibrational modes existed in the cement samples.

**Table 4.3** FTIR spectral band assigned to the vibrational modes of control GIC sample.

| Wavenumber ($cm^{-1}$) | Assignment of vibrational mode | References |
|---|---|---|
| ~440 | $v_2$ O-P-O bending mode | Mandal et al. (2014), Zarifah et al. (2016) |
| | Si-O-Si vibration mode | Jusoh et al. (2019), Rahman et al. (2019) |
| ~570, ~600 | $v_4$ O-P-O bending mode | Moshaverinia et al. (2008), Goenka et al. (2012), Garcia-Contreraset et al. (2015), Barandehard et al. (2016), Alatawi et al. (2019) |
| ~1020 | $v_3$ 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) |

According to Figure 4.6, several peaks appeared at wavenumber ~440, ~570, ~600, ~1020, ~1460, 103 ~1550 $cm^{-1}$ and a broad peak at range of ~3200 to 3400 $cm^{-1}$. The phosphate group in the apatite sample indicated that the spectral band at 440 $cm^{-1}$ belonged to either the double degenerate O-P-O bending mode ($v_2$), or the Si-O-Si vibration mode, as suggested by the use of SLS glass in the manufacturing of GIC cements. (Mandal et al., 2014; Zarifah et al., 2016; Jusoh et al., 2019; Rahman et al., 2019).

The triple degenerate O-P-O bending mode ($v_4$) then appeared at both intense peaks at wavenumbers of ~570 and ~600 $cm^{-1}$. Another occurrence of phosphate chemical bonding was found at a significant peak of ~1020 $cm^{-1}$, indicating asymmetric P-O stretching mode ($v_3$). The presence of a carbonate precursor in the formation of GIC samples was confirmed by the carbonate group, as demonstrated by the CO vibration mode at wavenumber ~1460 $cm^{-1}$.

Khiri et al. (2020) also highlighted how the carboxyl group in PAA used in the formulation of GIC resulted in the formation of an asymmetric COOH band at ~1550 $cm^{-1}$. The carboxylic group cross-linking reaction was seen in all cement samples due to an active reaction between PAA and ASF glass ceramics.

At a high frequency of 3400 $cm^{-1}$, a wide absorption band was detected, indicating that the OH vibration mode was present. Water absorption causes intermolecular H bonds to stretch, resulting in the vibrational mode, according to Jekonovic et al. (2013) and Montazeri et al. (2011). At the same time, the presence of this spectral band indicated that water had been present during the cement preparation process (Montazeri et al., 2011).

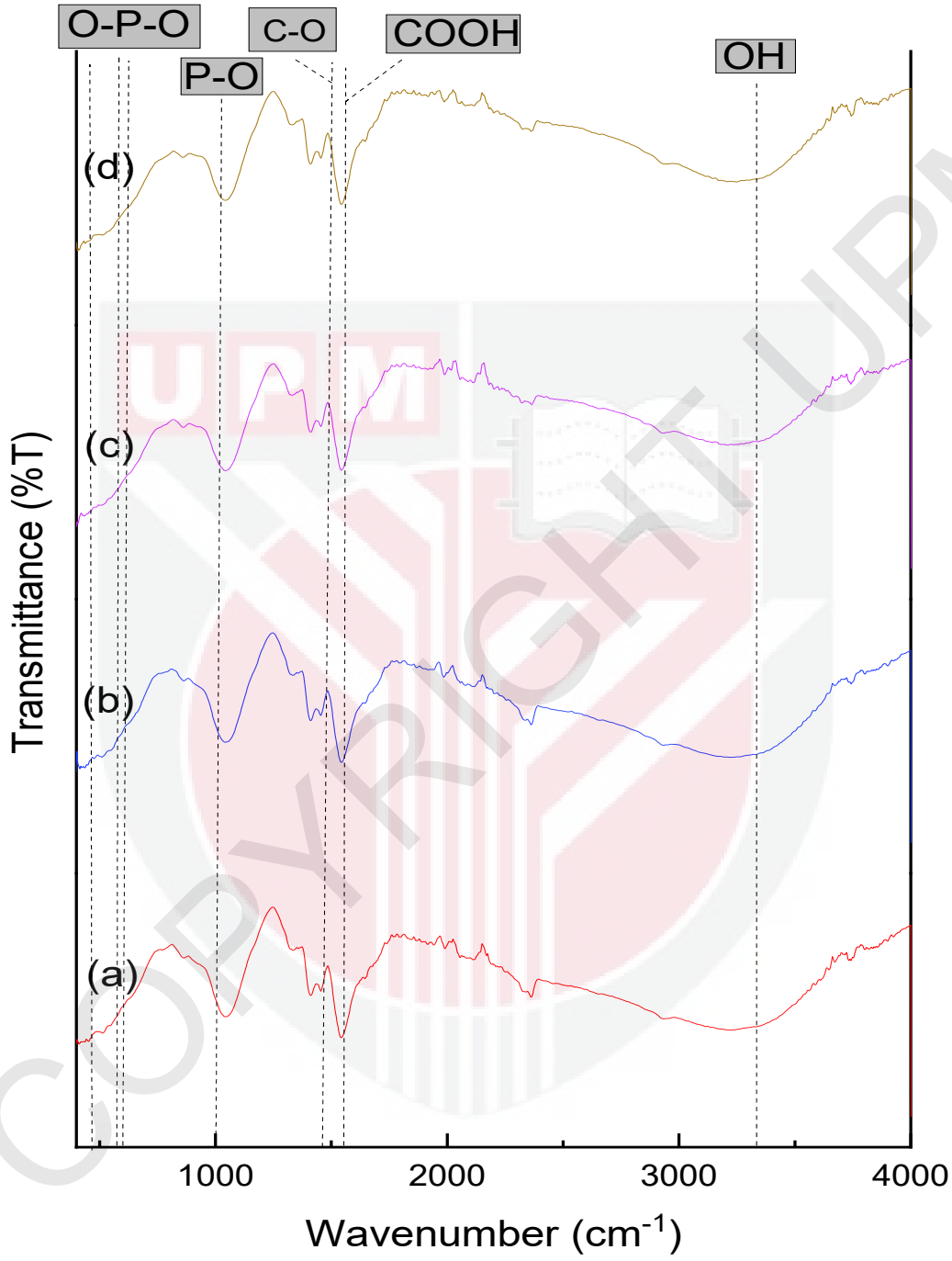



**Figure 4.6** FTIR pattern of GIC sample at (a) 7 days, (b) 14 days, (c) 21 days and (d) 28 days of ageing time.

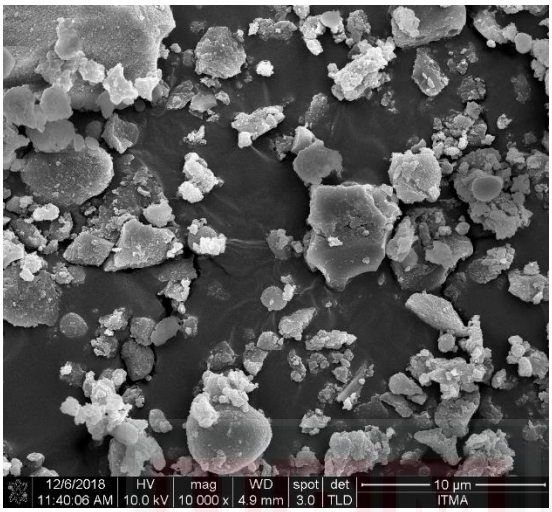
### 4.3.3 FESEM Analysis of GIC

The FESEM analysis was conducted to study the shape, size and morphology of the GIC samples. The morphology of GIC is shown in Figures 4.7 (a), (b), (c), and (d) at magnifications of 10 000x, 40 000x, and 200 000x. Figures 4.7 showed FESEM images of control GIC samples without heat treatment at ageing times of 7 days.

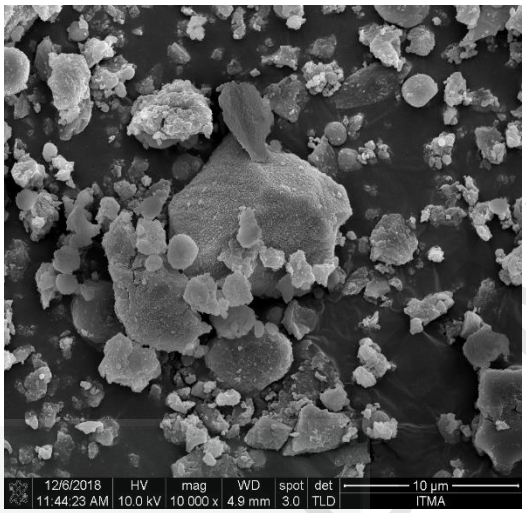
Figures 4.37(a) and (b) illustrate a granular and spherical shape with uniform microstructure distribution before sintering with a magnification of 10 000x. The apatite phase known as Fluorapatite in the GIC sample is indicated by granular and needle-like features available at low sintering temperatures.

In the sample illustrated in Figure 4.37(c) from FESEM analysis with magnification of 40 000x, a non-uniform particle distribution with irregular shape existed. Because ASF-based glass ceramics powder was used in the GIC manufacturing process, the irregular shape of the particle revealed some granular structure, showing that the particle is glass ceramic in nature.

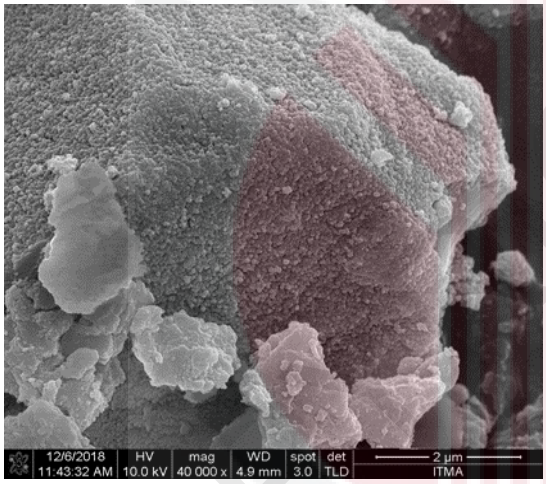
The structure that existed on the GIC samples was observed using a higher magnification FESEM. Images of GIC at a magnification of 200 000x were shown in Figure 4.37(d). The presence of apatite particles in the GIC formulation was supported by the presence of some agglomerated spherical particles in all samples.



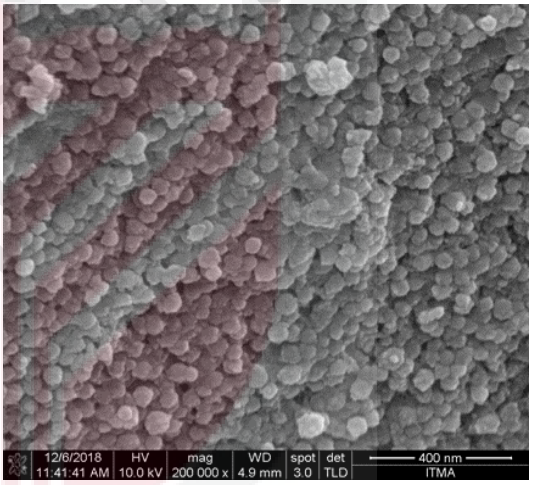

**(a) 10 000x**




**(b) 10 000x**




**(c) 40 000x**




**(d) 200 000x**

**Figure 4.7** FESEM micrograph of GIC at various magnification of (a) and (b) 10 000x, (c) 40 000x and (d) 200 000x for 7 days of ageing time.

# CHAPTER 5

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Introduction

The focus of this research is to examine the physical and structural properties of GIC made from waste materials utilizing ASF-based glass ceramics. In order to acquire a better knowledge of the final product of GIC, the crystallization process of ASF based glass ceramics is investigated in this work. GIC is then produced from ASF-based glass ceramics that have been aged for 1, 7, 14, 21, and 28 days. Density, XRD, FTIR, and FESEM were all used to examine the samples. The following conclusions in this part are based on the analytical results collected throughout the laboratory work.

## 5.2 Conclusions

In order to meet the goals of this research work, a number of conclusions have been reached. ASF-based glass ceramics have been successfully synthesized from waste materials comprising of CS and SLS glass, to name a few accomplishments. GIC samples were also successfully fabricated using an acid-base reaction involving ASF-based glass ceramics powder, deionized water, and PAA with a ratio of 3:1:1.

In addition, the influence of ASF-based glass ceramics on the physical and structural properties of GIC was studied in this research. Results for density of GIC samples based on different sintering temperatures and ageing times show no big changes. The density of GIC increases as the sintering temperature rises from 30 to 600 °C. After that,

at 700 °C and 900 °C, the density shows a decrement pattern. The highest density measurement of GIC is 1.844 g/cm$^3$ which is at 600 °C with ageing time of 21 days while the lowest density measurement of GIC is 1.585 g/cm$^3$ which is at 900 °C with ageing time of 1 day. This could be attributed to the development of new anorthite and mullite phases at high sintering temperatures. Fluorapatite is also identified as a major phase in the composition by XRD analysis. At high sintering temperatures, it decomposes into mullite and anorthite similar to the ASF glass ceramics sample.

In addition, the FTIR spectral revealed the development of $v_4$ O-P-O bending mode, C-O bond properties, $v_3$ asymmetric P-O stretching, C-O, and OH vibration modes. The presence of the crystal phase was confirmed by FTIR, which detected OH chemical bonding around 3400 cm$^{-1}$ in the spectrum wavenumber.

The appearance of agglomeration of spherical and needle-like particles in GIC samples was indicated by FESEM morphology of ASF glass ceramics, which confirmed the presence of apatite crystals in the samples. Furthermore, when the sintering temperature rises, the particle form becomes coarser. This is due to the phase transition process at high sintering temperatures.

Finally, due to the presence of fluorapatite in the glass structures, GIC is a promising candidate for clinical applications in dentistry. At high temperatures, the phase transition process caused GICs' physical qualities to deteriorate. However, because both phases (anorthite and mullite) have many advantages in dentistry, enhancements can be developed so that they can be employed in dental applications. In this research, GIC produced from ASF-based glass ceramics formed from CS and SLS glass were found to be beneficial in dentistry as luting, restorative, liner/base, and luting for orthodontic purposes.

## 5.3 Recommendations for future research

Some ideas for GIC's future work to have a better understanding of this topic have been made. To begin, the ageing time should be completed over a long period of time, such as one month to one year, in order to assess the GIC sample's endurance through time. Furthermore, different acidic polymer solutions, such as itaconic acid, maleic acid, and vinyl phosphonic acid, can also be used to make GIC. The acid content of the cement might have an impact on its toughness and mechanical properties. Next, the ratio used for glass, deionized water and polymer can be varied such as 4:2:2 to improve the physical and structural properties of GIC. Last but not least, other than using heat treatment, other additive elements can be added as a component of GIC such as HA.

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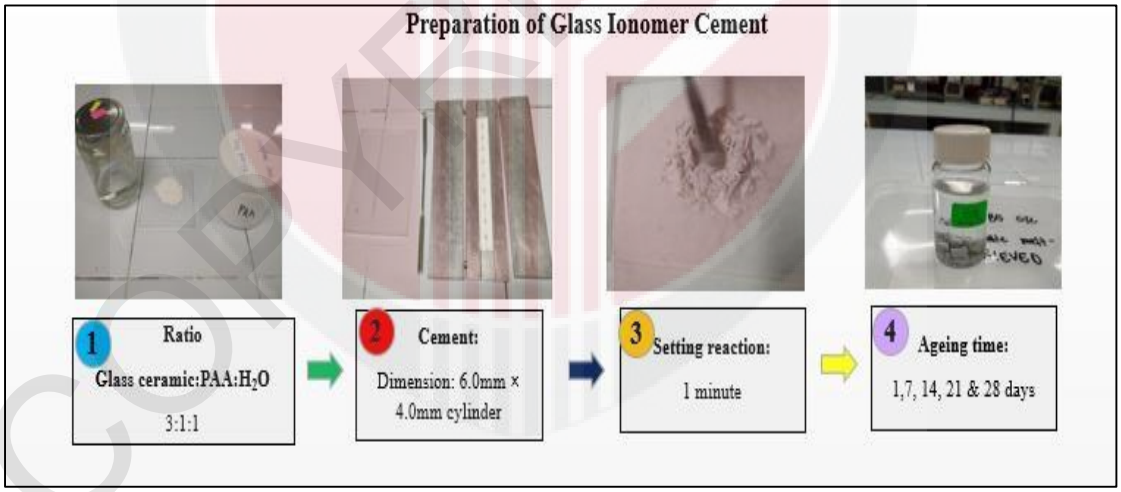
# APPENDICES

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| Institution | : Kolej Matrikulasi Negeri Sembilan (KMNS) |
| Year | : 2017-2018 |

**Sijil Pelajaran Malaysia (S.P.M)**

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| School | : SMK Aminuddin Baki |
| Year | : 2016 |

**Pentaksiran Tingkatan Tiga (PT3)**

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| School | : SMK Aminuddin Baki |
| Year | : 2014 |