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Comparative evaluation of the compressive strength, surface hardness and porosity of a selection of capsule-mixed versus hand-mixed Glass Ionomer cements

Dissertation submitted in fulfilment of the Degree of MSc (Dent) at the Department of Odontology, School of Dentistry, Faculty of Health Sciences, University of Pretoria, Pretoria, South Africa

Author: Dr Samantha Arnold

Student Number: 94395366

Contact details:

Tel: 012 319 2559

E-mail: Samantha.arnold@up.ac.za

Supervisor: Dr Paul Brandt, paul.brandt@up.ac.za

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Declaration and conflict of interest

I, Samantha Arnold, declare that this dissertation entitled "**Comparative evaluation of the compressive strength, surface hardness and porosity of a selection of capsule-mixed versus hand-mixed Glass Ionomer cements"** which I herewith submit to the University of Pretoria in fulfilment for the degree MSc (Dent) is my own original work.

Acknowledgement of all the resources I have used and/or quoted in this dissertation have been given, ether in the Acknowledgements section of this manuscript or in complete references that can be found at the end of this manuscript.

This work has never been submitted to any other institution of higher education.

Furthermore, I declare that I have no financial, commercial or any other associated interests that represents a conflict of interest with regards to the research undertaken and all other aspects related to the content of this manuscript.

Arnold

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Samantha Arnold
October 2019

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For the Spirit God gave us does not make us timid, but gives us power, love, and self-discipline.

2 Timothy 1:7

Abbreviations

% - percentage

ASPA - Alumino silicated polyacrylic acid

CS - compressive strength

FIXC - GC Fuji IX GP capsule-mix

FIXCLC - GC Fuji Coat LC

FIXH - GC Fuji IX GP hand-mix

g - gram/s

IQR - interquartile range

kg - kilogram/s

KMC - Ketac Molar Aplicap capsule-mix

KMH - Ketac Molar Easymix hand-mix

KUC - Ketac Unversal Aplicap capsule-mix

KUH - Ketac Universal hand-mix

kV - kilovolt

MIDRAD - Micro-focus X-ray Tomography Facility

µm micron

ml - millilitre/s

mm - millimetre/s

mm^3 cubic millimetre/s

mN - milli-Newton/s

MPa - mega-Pascal/s

N/mm^2 - Newton/square millimetre

NECSA - South African Nuclear Energy Corporation

nm - nanometre/s

RC - Riva Coat

rpm - revolutions per minute

RSCC - Riva Self Cure capsule-mix

RSCH - Riva Self Cure hand-mix

SD - standard deviation

sec - second/s

SEM - Scanning electron microscope

VHN - Vickers hardness number

Summary

Introduction: Glass ionomers are available in sets of powder and liquid constituents, which are dispensed using a scoop and dropper bottle system prior to hand-mixing by an operator. Glass ionomers are also available in capsulated form, which is mixed in a suitable mechanical mixing machine prior to clinical use. Capsulation enables uniform proportioning of the powder and liquid. In this context, mixing time will be correct as an automated process is utilised, resulting in a cement mixture that is optimal and reproducible, with minimal air entrapment. Manufacturers promote the capsulated form as being time saving, and easy to dispense, with more accurate adaptation because of the use of an applicator to place the material. **Aim:** The aim of this *in vitro* study was to compare the performance of hand-mixed glass ionomer materials with their capsule-mixed equivalents in terms of compressive strength, surface hardness and porosity. **Materials and Methods:** Four groups of 10 cylindrical specimens were manufactured for each of the four specified hand-mixed posterior glass ionomers for each test that was performed: Riva Self Cure (RSCH) (SDI Limited); GC Fuji IX GP (FIXH) (GC Corp); Ketac Universal (KUH) (3M ESPE) and Ketac Molar Easymix (KMH) (3M ESPE). Similarly, four groups of 10 cylindrical specimens were manufactured for each of the four equivalent capsule-mixed posterior glass ionomers for each test that was performed: Riva Self Cure (RSCC) (SDI Limited); GC Fuji IX GP (FIXC) (GC Corp); Ketac Universal Aplicap (KUC) (3M ESPE) and Ketac Molar Aplicap (KMC) (3M ESPE). The compressive fracture strength of each specimen was determined after 24 hours using a universal testing apparatus. A compressive load of 1 mm/min was applied to the 6 mm long axis of each specimen. The load to fracture was recorded and the compressive fracture strength was calculated. Within one hour after compressive strength testing, a selection of fragments from each specimen was examined by Scanning Electron Microscope (SEM).

Fragments were vacuum gold-sputter-coated prior to SEM examination. The fragments were observed at an operating voltage of 10kV, and over a range of magnifications to investigate crack propagation. The surface hardness of each specimen was measured with a digital micro-hardness tester with Vickers diamond indenter. The indenter was set at a load of 500mN at five predetermined regions of each specimen, with a dwell-time of five seconds. The five readings for each specimen were computed and the mean VHN in N/mm^2 for each specimen was determined. Each specimen was observed and analysed for porosity using Micro-CT. Three-dimensional reconstructions were made of each specimen and the number of voids per volume (mm^3) of specimen, the total volume of voids (mm^3) per volume of specimen and the volume percentage of voids per volume of specimen were calculated. **Results:** RSCH and RSCC showed statistically significant differences when compressive strength (p=0.027), volume of voids (p=0.005) and volume percentage of voids (p=0.005) were compared. No statistically significant differences were found between RSCH and RSCC when surface hardness (p=0.124) and number of voids (p=0.221) were compared. When compressive strength (p=0.254) and number of voids (p=0.210) of FIXH and FIXC were compared, no statistically significant differences were found. Statistically significant differences were found when surface hardness (p=0.031), volume of voids (p<0.001) and volume percentage of voids (p<0.001) of FIXH and FIXH were compared. No statistically significant difference was found when compressive strength (p=0.090) of KUH and KUC were compared. Statistically significant differences were found when surface hardness (p<0.001), number of voids (p<0.001), volume of voids (p=0.004) and volume percentage of voids (p=0.004) of KUH and KUC were compared. Statistically significant differences were found between KMH and KMC when compressive strength (p<0.001), surface hardness (p=0.006), number of voids (p=0.001), volume of voids (p=0.010) and volume percentage of voids (p=0.010) were compared.

Conclusion: The current study suggests that RSCC is more advantageous for clinical use compared to RSCH. The results as to whether the capsule-mix or the hand-mix product are superior for the examined properties for GC Fuji IX GP are inconclusive. KUC surpassed KUH in tests performed and is therefore recommended for clinical use. KMC out-performed KMH in all tests conducted, and is therefore advocated for use in clinical practice.

Key words

Glass ionomers

Hand-mix

Capsule-mix

Compressive strength

Surface hardness

Porosity

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Appendix A: Ethical clearance

Chapter 1: Introduction and Literature Review

Extensive research has been carried out on glass ionomer cements in an effort to find a suitable alternative aesthetic posterior restorative material to overcome the deficiencies of composite resin materials.[1] Improvements in the tensile strength, compressive strength and wear resistance of glass ionomers have been made.[2,3] Advancements in aesthetics, bonding, fluoride release, anti-bacterial activity and pack-ability have also taken place.[4]

Glass ionomer cements bond chemically to the calcium in the hydroxyapatite of tooth structure. These cements are not subject to polymerization shrinkage, and have a coefficient of thermal expansion similar to tooth structure.[1,5] Glass ionomer cements release fluoride and are also capable of fluoride re-uptake from food and oral care products.[5,6] The aforementioned positive attributes of this dental material are reinforced by the biocompatible nature of these dental cements, which makes them undeniably advantageous for dental use.[5,6]

Glass ionomers are available in powder and liquid constituents, which are dispensed using a scoop and a dropper bottle system prior to hand-mixing of the material by an operator. Glass ionomers are also available in capsulated form which must be mixed in a suitable mechanical mixing machine.

Capsulation enables uniform proportioning of the powder and liquid parts of the dental glass ionomer.[7] Mixing time is correct as it is an automated process, resulting in a cement mixture that is optimal and reproducible, with minimal air entrapment.[7,8] Manufacturers promote the capsulated form of these glass ionomer cements as being easy to dispense, more time-efficient and it leads to more accurate adaptation because of the use of an applicator to place the material.[8,9]

In this study, both the hand-mixed and capsule-mixed versions of four glass ionomer restorative materials, from three different manufacturers, were selected. The compressive strength, surface hardness and porosity of these products were measured and these properties were compared.

The outcome of this present study aimed to determine whether the capsule-mixed form of each glass ionomer is superior to the equivalent hand-mixed product, in terms of: compressive strength, surface hardness and porosity.

To the best of the researchers' knowledge, this was the first *in vitro* study undertaken in South Africa, to compare the compressive strength, surface hardness and porosity of hand-mixed and capsule-mixed glass ionomer restorative materials.

Furthermore, to the best of the researchers' knowledge, this was the first study carried out in South Africa to assess the porosity of glass ionomer restoratives with the XTH 225kV Micro-focus X-ray/CT system of Nikon Metrology (Leuven, Belgium) at the Micro-focus X-ray radiography/ tomography facility (MIXRAD) of the South African Nuclear Energy Corporation (NECSA). The knowledge and experience gained from the research undertaken at NECSA will be used in the future for testing similar parameters of a variety of other dental materials.

The results of this research will also provide valuable information to dental practitioners in selecting the most suitable glass ionomer restorative of either hand-mixed or capsule-mix versions, as applicable to their specific clinical needs.

1.1 The Historical Evolution of Glass Ionomer cements

In 1962, research done by Bowen leads to the manufacturing of bis-GMA, a reaction product between glycidyl methacrylate and bisphenol A.[1] This crucial discovery was the key to the introduction of resin composite as a restorative material in the dental profession in the 1960's.[1,10]

Resin composite proved to have a wide range of applications in restorative dentistry. The advantages of resin composite over the existing materials that were available on the market at that time were numerous. Resin composite is aesthetic, insoluble once fully set and able to endure occlusal forces.[1] It also requires minimally invasive cavity preparation and is also relatively cost-effective when compared to indirect restorations.[1,11]

The indications for the use of resin composites in dentistry include anterior and posterior restorations, pit and fissure sealants, cavity liners, core build-up materials, direct and indirect inlays, overlays and crowns and luting cements for orthodontic and prosthetic treatment.[10] These materials are not without challenges as they undergo shrinkage during the process of polymerization. Not only can this factor cause internal stress within the placed restorative material, it can also create shrinkage-related stress on the adhesive bond between the restorative material and the adjacent tooth structure. This shrinkage stress is directly transferred to the tooth structure.[10,12] Polymerization shrinkage of resin composite is linked to micro-leakage, marginal discrepancies, cusp fractures, post-operative pain and secondary caries.[10,13]

Resin composite relies completely on an adhesive bonding system for retention to tooth structure.[10] The success of a resin composite is dependent on meticulous clinical technique and ideal restorative conditions.[10]

The incremental layering of resin composite in layers of two millimetres or less, is of utmost importance to limit the amount of polymerization shrinkage and shrinkage stress associated with this phenomenon.[10,12]

Dental research into alternative dental restorative materials which display the lowest possible polymerization shrinkage, which chemically bonds to tooth structure without additional adhesive systems, and can be placed in bulk, has been ongoing. Glass ionomer cement meets these criteria.

The discovery of glass ionomer dental cements was not incidental. A series of scientific studies, experimenting with dental silicate cements were initiated in the early 1960's.[3,14] In general, the dental silicate cements comprised mainly of an alumino-silicate glass powder and a liquid of phosphoric acid, which when combined, set by an acid-based reaction.[14,15]

In the 1960's, dental silicate cements were the material of choice for anterior dental restorations as they were the most translucent dental material available. Unfortunately these cements were unable to adhesively bond to tooth structure, were brittle, likely to erode and stain, and had a tendency to cause pulpal sensitivity.[3,14,15] The lack of understanding of the chemistry of the dental silicate cements were a major obstacle for researchers at this point in time, this despite the fact that this dental material had been in use for over 50 years.[14]

Extensive studies on dental silicate cements were initiated at the London Government Chemist (LGC) by Wilson and Batchelor in 1964.[16,17] Leaching experiments led to the discovery that aluminium and calcium phosphates form part of the dental silicate cement matrix. It was anticipated that phosphate probably played an imperative role in the setting reaction, thus researchers suggested replacement of phosphoric acid with a less aggressive, organic chelating acid, which could similarly interact with the tooth's hydroxyapatite.[14]

Experimental cements were prepared by mixing a number of acids, including tartaric acid, pyruvic acid, tannic acid, fluoboric acid, glycerol phosphoric acid and tetraphosphoric acid (at concentrations ranging from 35 to 50 %), with the alumino-silicate glass powder which is used in dental silicate cements. The resulting cements had good handling and working properties and set between two to eight minutes, but were hydrolytically unstable, with some totally disintegrating.[3,14] Polyacrylic acid at a 25 % concentration was also included in these experiments. The cement which formed from this polyacrylic acid mixture was hydrydrolitically stable when allowed to set for 24 hours, but had little or no working time.[14] Polyacrylic-, phytic- and polyvinylphosphonic acid were capable of forming hydrolytically stable cements, but the addition of a third-component was necessary to ensure adequate setting.[3,14] It seemed apparent that no two-component mixtures of alumina-silicate glass powder in combination with a chelating acid were capable of rendering a workable dental cement.[14]

Research about dental silicate cements were resumed by Wilson and Kent in 1968.[14] Soon they discovered that the alumina to silica ratio possibly controlled the reactivity of the glass component as well as the setting time.[3,14,18] The alumina to silica ratio in the experimental cements were increased to at least 0.57 (the previous studies used 0.5), in the follow-up studies. They also decided to increase the concentration of polyacrylic acid in the liquid to between 40 and 50 %.[14] The cements formed from these combinations set within five minutes. The working time was still, however, not long enough and maturation rates of the material were still too slow.[14] Further work on this particular cement brought about sufficient improvement for clinical use and this material was patented in 1969 by the National Research Development Corporation (now the British Technology Group).[3,14] The name ASPA, an acronym for AluminoSilicated PolyAcrylic acid, was given to this cement.

The evolution of glass ionomer cement continued, as a new glass powder was formulated during experiments investigating the effect of alternative glass combinations on cement properties. This new G-200 glass powder formulation was superior to the alumina-silicate glass powder used in ASPA, due to the high fluoride and calcium content in addition to aluminium and silica.[3,14] Cements that were made from G-200 glass had much better working time, strength and resistance to moisture than any cement before, and was christened ASPA I. The success of ASPA I was attributed to the high fluoride content of the glass powder.[14] Alumino-fluoride complexes would temporarily withheld aluminium ions from the polymer chains during the chemical reaction, thereby increasing the working time.[14] John McLean, the clinical consultant during the development of these glass ionomers, found ASPA I to be clinically useable, but the slow setting, limited working time and poor aesthetics were problematic.[3,14]

Wilson *et al*.[19], undertook research to attempt to improve the setting characteristics of ASPA I. This research investigated the addition of another chelating agent as third component.[19] This third chelating agent could possibly control the setting reaction by delaying or preventing the precipitation of aluminium. Many different chelating agents, including citric acid, salicyclic acid, acetylone, sequestric acid, polyglycol and tartaric acid were incorporated into the ASPA I formulation. Tartaric acid surpassed all expectations, by increasing the working time[19], compressive fracture strength[20] and resistance to acid dissolution[14] and at the same time shortening the setting time.[14,19,20,21] This modified version of ASPA I was named as ASPA II, which contained G-200 glass, tartaric acid and polyacrylic acid. ASPA II was mainly used as a dental sealant for pits and fissures.[22]. This limitation of clinical application was due to the inferior aesthetics as compared to that of composite resin materials.[3,14] The clinical use of ASPA II for Class III and Class V restorations at that stage was minimal.[14]

At this point changes had to be made to the liquid component of ASPA II because of the gelation of the polyacrylic acid homopolymer.[23] Crisp *et al.*[24] suggested a methanol containing modification and this product was referred to as ASPA III.[24,25] Later a version of this product containing a copolymer of acrylic and itaconic acid, was produced, which was called ASPA IV.[24,25]

In 1975, ASPA IV was the first commercial hand-mixed glass ionomer material launched by the Amalgamated Dental Company (Dentsply DeTrey, Konstanz, Germany) under the trade name ASPA.[3,26] Mount and Makinson[27] conducted a study where five dental nurses and one dentist were asked to hand-mix the ASPA according to the manufacturer's specifications. On average the operators were only able to incorporate 85 % (by weight) of the powder content, although powder content as low as 42 % was noted in some samples.[27] This study confirmed that the powder/liquid mixing ratios obtained by operators were below that which had been specified by the manufacturer. As a result of this research, Dentsply DeTrey made an encapsulated version of ASPA available on the market in 1978. The hope was that encapsulation would avoid operator variability in powder and liquid proportioning.[3]

In the years following the introduction of ASPA, a number of modifications were made to glass ionomer cements in attempts to enhance the material's mechanical properties.[3,28] As already mentioned, these included the use of alternative polymers such as acrylic acid, maleic acid and polyvinylphosphoric acid as part of the liquid.[3,28] Experimental fillers were also added to the glass powder including ceramic-metal fillers; metallic powders such as silver-tin alloy and stainless steel; carbon and alumina fibres; hydroxyapatite powders; bioactive glass particles and montmorillonite clay.[3,28]

Hybrid formulations of traditional glass ionomers have also been marketed since the late 1980's.[29] Light-curing resin, HEMA in most studies, in different quantities were added to traditional glass ionomers to increase the wear resistance and strength and improve the aesthetics.[30] These hybrids include Resin Modified Glass Ionomers and Polyacid Modified Resins or Compomers.[30]

Modern high viscosity glass ionomers have recently been introduced on the dental market. These cements show increased resistance to stress and superior hardness which can be attributed to the structural changes made possible by nano- technology.[4,30] The aesthetics, fluoride release and re-uptake of fluoride from food and oral care products (i.e. topical fluoride gel applications, fluoride containing toothpastes and mouth rinses), of these cements are also significantly enhanced.[4]

1.2 Composition of modern conventional Glass Ionomer cements

Ion-leachable glass

The glass powder used for glass ionomer cements are prepared by melting powdered silica (SiO_2), alumina (Al_2O_3), cryolite (Na_3AlF_6), aluminium trifluoride (AlF_3), fluorite (CaF_2) and aluminium phosphate ($AlPO_4$) at 1100 to1500 degrees Celsius.[3] This melted glass is then shock cooled with water. The resultant course glass frit is ground using a ball mill and then sieved to form a powder. The size of the particles depends on the intended application of the glass ionomer cement. The particle size is a maximum of 45μm for a restorative glass ionomer cement and 15μm for a glass ionomer luting cement.[3,28]

Most of the modern commercial glasses contain strontium, barium and lanthanum ions.[3,31] These elements are added to increase the radiopacity, making detection of the glass ionomer on radiographs easier. Strontium can also substitute calcium in the composition of the glass powder because of the similar ionic radius.[3] Strontium oxide (SrO) and strontium trifluoride (SrF_3) will then replace calcium oxide (CaO) and fluorite (CaF_2) in the glass-forming mixture.[3,31] Thus the radiopacity of the glass ionomer can be improved without disrupting the glass network or losing the translucency of the glass. Research has also shown that fluoride release from strontium substituted glass ionomers are increased. The reason for this fact is still unclear.[31]

Some of the latest available glass ionomer cements contain zinc (Zn) as part of the powder composition to increase the strength of the material by up to 25 %.[32]

Polymeric water soluble acid

Polymers used in glass ionomers are polyalkenoic acids, either homopolymer polyacrylic acid or the 2:1 copopymer of acrylic and maleic acids.[31] One product uses polyvinyl phosphoric acid mixed with polyacrylic acid, which effectively acts as a setting rate modifier.[31]

The molecular weight of the polymers used influences the strength and viscosity of the glass ionomer cement.[31] The higher the molecular weight of the polymers, the stronger the product, however, viscosity increases, making the product difficult to work with.[31] Average polymer molecular weights of 11,000 (number average) and 52,000 (mass average) will result in optimum properties of a glass ionomer cement.[33,34]

Research has shown that the compressive strength of cements increase in the first four to six weeks when homopolymers of acrylic acid is used.[31] Cements prepared with copolymers of acrylic-maleic acid show an increase in compressive strength up to a point, then decline before an equilibrium value is reached.[31] This fact indicates that the materials continue to undergo changes as time progresses. The reduction has been explained by the higher crosslink density that develops within the copolymer cements, compared to that of acrylic acid homopolymer cements.[28,31] However, in clinical use, there is no evidence that cements prepared from acrylic-maleic acid copolymer are inferior to acrylic acid homopolymers.[31]

Water and chelating additives

Water serves as the solvent for the polymeric acid and also as the reaction medium, promoting proton release and transportation of ions to react with the polyalkenoic acids.[6,28,31] Water is an essential component of the set cement, hydrating the siliceous hydrogel and the metal salts that are formed.[6] If water is lost from the cement by desiccation while setting, the cement forming reaction will stop.[28,31] A freshly placed glass ionomer restoration can lose unbound water, which causes a chalky appearance, because the drying surface develops microscopic cracks.[31] It is imperative that the cement is covered with the product-specific varnish or petroleum jelly directly after placement in order to prevent dehydration.[31,35] Light-curable varnishes, with low viscosity monomers, give superior protection against dehydration.[31] The cured varnish has minimal porosities which prevents water from escaping.[31]

Tartaric acid or citric acid at either five or ten percent by mass, are used as rate-modifying additives.[20] Tartaric acid has been proven to be more successful, but the reason for this is unclear. The most likely answer would be that tartaric acid prevents the precipitation of aluminium salts by chelation of aluminium (Al^{3+}) ions, thus keeping the ions in solution and preventing the premature formation of ionic crosslinking involving Al^{3+}.[31,36,37]

Tartaric acid initially delays the setting of the cement, making the cement easier to mix, it then causes rapid setting of the cement allowing the operator to finish the hardened product.[6] The effectiveness of tartaric acid is dependent on the glass composition used.[31,37] Tartaric acid also improves the translucency of the material, improving the aesthetics.[6]

1.3 Presentational forms of Glass Ionomer cements

Two presentational forms of glass ionomers are currently available from dental material manufacturers.

The first form is presented as a separate glass powder and separate polyalkenoic acidic liquid that must be mixed by hand and is set by an acid–base reaction.[38,39]

The second form is the capsulated form, which is mixed in a mechanical mixing machine, initiating the acid-base reaction.[39] The capsule contains a blend of glass powder and vacuum-dried polyalkenoic acid,[38,39,40] with a separate compartment containing either distilled/deionised water or a solution of tartaric acid and water.[3,38]

The capsulated glass ionomer cements are more costly per application in comparison to the equivalent hand-mixed versions.[41] It is most likely for this reason that some private dental practices elect to use hand-mixed glass ionomer cements rather than capsule-mixed glass ionomer cements.[41]

Operator variability is the leading cause of inconsistency of hand-mixed glass ionomer materials.[39,41,42,43,44,45,46,47] Measuring systems are provided by the manufacturers in the form of powder scoops and liquid dropper bottles.[3] Powder density and the technique of the operator can influence the volume of powder dispensed when filling the scoop.[41]

The angle at which the bottle is held and the pressure applied by the operator to squeeze the bottle, leads to un-calibrated volumes of liquid dispensed.[38,39,40,42,43,44,48] Air bubbles in the liquid are often seen and will influence the volume of liquid dispensed.[41] Both the mixing time and cement manipulation technique contributes to operator induced variability.[41] In addition, the humidity and temperature in the mixing environment may influence the cement consistency.[41]

In clinical practice the problem is made worse as scoops and dropper bottle systems are often not used, the product is mixed to the operators' or dentists' desired consistency,[38,43,44] resulting in hand-mixed cement that does not meet the ideal characteristic that is possible to achieve, when mixed according to manufacturers' instructions.[41,43,44,45,49] The resulting material will be weaker, with altered chemical, mechanical and physical properties,[41,43] and setting time.[41] Acid erosion of the restoration is also more likely.[41]

Billington *et al.*[43] investigated the effect of different glass ionomer luting cement powder volumes at 50 %, 80 %, and 90 % of the powder content recommended by manufacturers, hand-mixed with a fixed one millilitre volume of liquid. This study was done to prove the result of operator variability and also indicate the effect of dentists' preference of consistency on the strength of the mixed cement.[43] Compressive strength and diametral tensile strength of the different consistencies of mixed cement, were lower and did not meet the requirements for the British Standard.[43] Flemming *et al.*[41] carried out a similar study of a posterior restorative glass ionomer at different powder volumes, mixed with a constant volume of liquid. The study concluded that the glass filler particles within a mixed cement reinforces the matrix and gives resistance to compressive loading stress.[41] The less powder added to the liquid, the lower the compressive strength due to the lower glass filler content.[41] By SEM investigation it was found that the lower the powder content of the mixed cement, the lower the levels of porosity.[41] Increased spatulation pressure when hand-mixing with increased powder volume to constant liquid volume, was most likely the cause of increased porosity seen in specimens with higher volumes of powder content.[41] Lowering the powder volume to a fixed liquid volume, resulted in prolonged working and setting times.[41]

Capsulation of glass ionomer cements have the advantage that they are pre-proportioned at a set powder/liquid ratio and the mixing technique and times are standardised.[38,42,50,51] These products seem to be more user friendly and time saving.[8,9] The mixed cement is immediately injected into the prepared cavity directly from the capsule.[51]

Research has, however, shown that the vibratory action of conventional mechanical mixing machines does lead to increased porosity of some capsulated glass ionomers cements compared to their hand-mixed equivalents, leading to weakening of the cement.[7,50,51,52,53] Mechanical mixing machines with combined rotational and centrifugal action are advocated by some manufacturers and researchers to reduce porosity formation.[38,47] Research conducted by Fleming *et al.*[47] and Dowling and Fleming[38] showed that these types of mixing machines do not offer benefits. Porosity within the cement act as a source of stress concentration, negatively affecting the strength and homogeneity of the material.[51,52,54]

Prentice *et al.*[55] experimented with the mixing times of encapsulated glass ionomer cement. It was found that mixing the capsule for eight to ten seconds delivered a product with optimal strength and handling properties. Decreasing the mixing time was shown to prolong the working time and the setting time.[55] Increasing the mixing time led to increased viscosity of the material and reduced both the working and setting time.[55] The specimens that were mixed for 12 sec showed an increase in modulus of elasticity and compressive strength.[55] Gelation occurred too quickly with a mixing time of 14 sec, making the expression and placement of the material difficult due to the material pre-gelling.[55] The modulus of elasticity and compressive strength decreased for the specimens mixed for 14 sec.[55] In busy private practices the dentists might be tempted to take advantage of the increased viscosity and decreased working and setting time of longer mixed capsulated glass ionomer cement, but that might negatively affect the mechanical properties of the final cement.[55]

Scientific literature shows conflicting evidence on whether the capsulated-mixed glass ionomers are in fact of higher quality than the hand-mixed glass ionomers, or not.[7]

Nomoto and McCabe[51] experimented by hand-mixing the contents from a capsule of a low viscosity encapsulated glass ionomer luting cement, which has a relatively low powder/liquid ratio, in comparison to the equivalent hand-mixed low viscosity glass ionomer luting cement. The strength of the resulting product was similar to that of the equivalent hand-mixed product, which has a higher powder/liquid ratio in comparison.[51] These researchers also placed the powder and liquid of the equivalent hand-mixed glass ionomer luting cement into a capsules and mixed them in a mechanical mixing device. The resulting product was found to be much weaker in comparison to the end product of this same material had it been mixed by hand as recommended by the manufacturer.[51] The results of this work suggest that the differences in the properties of the mixed products are not only related to the powder/liquid ratios, but also to the viscosity and mixing methods employed.[41,51]

Nomoto and McCabe[51] also proved that the extent to which the porosity is managed, by the method of mixing, can result in the meaningful alteration of the properties of a set glass ionomer cement.

Voids or porosity are either incorporated by air entrapment or by inadequate wetting of the powder and liquid when mixing.[51] Large voids are responsible for material failure at low levels of stress.[51] Mitchell and Douglas[53] conducted research on the porosity of hand-mixed and capsule-mixed glass ionomer luting cement. It was found that hand-mixed luting cement contained more voids and voids with a larger diameter than their capsule-mixed equivalent.[53] They attributed the decreased strength of the hand-mixed cement to the presence of these voids that had been incorporated during the mixing process.[53] A study done by Kaushik *et al.*[52] proved to the contrary, that hand-mixed glass ionomers had fewer voids per surface area compared to the equivalent capsule-mixed version.

White and Zhaokun[56] reported that the compressive and tensile strengths of capsule-mixed glass ionomer luting cements were lower than compared to the hand-mixed equivalents made by the same manufacturer. Mitchell *et al.*[57] published an article in 1994 on post pull out tests when using different glass ionomer luting cements. The tests showed that capsulated cement failed at noticeable lower loads when compared to hand-mixed cement.[57] Later in 1998 Mitchell *et al.*[58] published a paper on the effect of the mixing method on glass ionomer luting cements used for post retention. They recommended the use of capsule-mixed cements, as the probability of survival was shown to be higher if posts cemented with capsule-mixed cements were subjected to a given load, when compared to the equivalent hand-mixed formulations.[58]

In 2001, Nomoto and McCabe[51] showed that lower viscosity glass ionomer luting cement had a greater mean strength when it was hand-mixed. It was suggested that hand-mixing reduces porosity in low viscosity glass ionomer cement as the material is spatulated by pressing downward, while the mechanical mixing machine introduces a type of a 'froth', 'fizz' or foam in low viscosity glass ionomer luting material.[51] SEM investigation of the low strength low viscosity mechanical mixed glass ionomer luting cement fragments showed large voids, which suggests that the low compressive strength of these specimens are due to the large voids present.[51] Mechanical mixing combined with centrifuging resulted in greater strength of encapsulated glass ionomer luting cement, when compared to the hand-mixed equivalents, as voids are forced to the surface and allowed to escape during centrifuging.[51] The effect of centrifuging is only advantageous as long as the material is still semi-fluid.[51]

In a study carried out by Nomoto *et al.*[50] in 2004, low viscosity glass ionomer luting cement was found to have more large voids when it was mechanically mixed. It was deduced that the cause might be the combination of smaller voids into larger voids until a certain viscosity is reached during setting.[50] For high viscosity glass ionomer cements the concentration of glass filler is higher and the chance of air entrapment less during mixing.[51]

Dowling and Flemming[38] have published extensive research on glass ionomer cements and advocate the use of capsule-mixed glass ionomer restoratives with respect to the superior mechanical properties of the mixed product. In their research they compared capsule-mixed glass ionomers with hand-mixed glass ionomers of different powder/liquid ratios as encountered in clinical practice. From the results they recommend capsule-mixing of glass ionomer cements as a solution to operator induced variability of the hand-mixed glass ionomer cements.[38]

The mixing method of glass ionomer cements could influence the fluoride release profile. Research undertaken by De Moor *et al.*[59] proved that mechanical mixing of glass ionomer cements in capsule form had a more predictable fluoride release profile, as opposed to hand-mixed glass ionomers.[59] The amount of fluoride release is dependent on the acid-base and setting reaction and therefore indirectly implies that both reactions are more uniform and reproducible with capsule-mixed glass ionomers.[59]

1.4 Setting reaction of Glass Ionomer cements

Glass Ionomer cements set through an acid-base reaction. The average setting time is within two to three minutes.[31] As soon as mixing is initiated, hydrated protons from the polyalkenoic acids react with the surface of the glass particles at basic (alkaline) sites. Firstly sodium-, calcium-, and strontium-ions move from the glass particles into the polyalkenoic acid solution, aluminium follows quickly thereafter.[31,60] Ionic crosslinking takes place between the free ions and the polyalkenoic acid molecules, resulting in the insoluble polysalt which forms the rigid framework of the set cement.[31] As the water is incorporated into the set cement there is no phase separation.[31]

The overall reaction seems to take place in a two phase diffusion-controlled process.[61,62] Various spectroscopic techniques, such as Infrared and Fourier Transform Infrared Spectroscopy (FTIR) have been used to study the setting of glass ionomer cements.[31,61] In the first phase, ionic crosslinks are formed and this is responsible for the immediate hardening process. The second phase involves a crosslinking process of aluminium ions, which occurs slowly (approximately 24 hours).[63] This crosslinking takes about 10 min to be spectroscopically identifiable.[31,64]

After the initial hardening, a slow maturation reaction takes place.[31] The strength, translucency and the proportion of tight-bound water within the structure increases.[31,65] The exact explanation for this process is still not known and research on this topic is ongoing.[31]

The set cement consists of un-reacted glass particles in a siliceous gel, which are fixed in a polyacid–salt matrix.[62]

The speed of setting and the ultimate strength of the glass ionomer restoration depends on the powder/liquid ratio of the components, the concentration and the molar mass of the polyacid and the presence of chelating agents.[6]

1.5 Adhesion of Glass Ionomer cements to tooth structure

Prior to the application of the glass ionomer cement, the tooth surface is conditioned with an aqueous solution of polyacrylic acid with a weak concentration.[66] This solution is left for 10 to 20 sec before being rinsed off with water.[31,66,67] This technique removes the smear layer, leaving enough available calcium in the tooth structure to allow chemical bonding of the glass ionomer to the tooth structure.[66] This also increases the surface area of the prepared tooth structure for bonding, improving the micro-mechanical attachment.[66,68]

The process of adhesion takes place in a few stages.[31] Proper wetting of the tooth surface by the fresh cement paste is facilitated by the hydrophilic nature of both the cement and the tooth structure.[31] Rapid adhesion then starts as hydrogen bonds form between the free carboxyl groups of the cement and the bound water on the surface of the tooth. As this process continues, hydrogen bonds are slowly replaced by true ionic bonds formed between the cations of the tooth structure and the anionic functional groups of the cement.[31] The molecular surface of the tooth's dental apatite structure is infiltrated by polyalkenoate chains which replace phosphate ions.[69] Calcium ions are displaced equally with the phosphate ions to reach an equilibrium.[68,69] This leads to the formation of an iron-enriched layer of cement which is firmly attached to the tooth structure, as has been illustrated by infrared spectroscopy.[31,62,69,70] Collagen from the tooth structure is not a component involved in the bonding process.[31,70]

The micromechanical interlocking of glass ionomers is made possible by the self-etching polyacrylic acid component of this dental material. True chemical bonding is achieved by the ionic bonds which are formed between the carboxylate groups on the polyalkenoic acid molecules and the calcium ions in the tooth structure.[68]

Strong adhesion of the cement to the tooth surface is achieved over time as "an ion-exchange zone" is created between the cement and the tooth structure, where ions move from both the cement and tooth. The exact nature of this "zone" it still not known, but it most likely consists of degraded apatite (from the tooth structure), with some phosphate in the tooth structure being replaced by polycarboxylate and glass ions.[71] This "zone" has been identified and can be seen using scanning electron microscopy.[71]

The tensile bond strength between glass ionomers to both untreated enamel and untreated dentine is good.[60] Bond strength values vary from 2.6 to 9.6 MPa to enamel and 1.1 to 4.1 MPa to dentine. These values suggest that bonding takes place during the mineral phase.[67] Within 15 min, 80 % of the final anticipated bond strength is achieved. The bond strength increases over several days thereafter.[67]

1.6 Advantages of Glass Ionomer cements

Glass Ionomer cements have the unique ability to chemically bond to tooth structure.[1] This aspect of the material ensures excellent marginal adaptation and seal between the set cement and the tooth structure, preventing micro-leakage.[5,31]

It also eliminates the use of bonding systems as with resin composite restorations, making the products less technique sensitive[66] and more cost effective. Furthermore a strong chemical bond allows for conservative cavity preparation with preservation of natural tooth structure and thus increased coronal strength.[72,73]

Glass ionomers release fluoride and are thus referred to as an anti-cariogenic material as this results in their ability to inhibit secondary caries formation.[6,30,65,74] The fluoride release takes place for quite an extensive period,[6,74,75] with rapid high release initially, followed by a lower sustained diffused release.[59,76,77] Glass ionomers with nano-sized particles show amplified fluoride release.[78] The release of fluoride from glass ionomers is also accelerated in acidic conditions.[79]

Newly placed glass ionomer restorations are able to absorb fluoride from saliva when present in the mouth from: dentifrices, mouth rinses, food and topical fluoride applications.[6,80] Unfortunately, the fluoride recharge potential declines with the maturation of the restoration.[77,81]

Apart from fluoride, glass ionomers are also able to release calcium and aluminium which both aid in the re-mineralization of tooth structure.[6] The bioactive ability of these ions is also thought to buffer the lactic acid of active caries (pH of 4.5), by increasing the pH of the external medium to 5.5, which may aid in protecting the tooth from further decay.[6,79,82]

Glass ionomers are placed in bulk as they do not undergo polymerization shrinkage and are self-curing.[6,72,83]

The material also has a co-efficient of thermal expansion similar to tooth structure, eliminating the possibility of the material causing internal tension within the tooth structure.[6,54,75]

Glass ionomer cements have a low toxicity and are biocompatible with the dental pulp and surrounding soft tissue.[6,54,72,82,84]

This material is highly radiopaque because of the addition of strontium, barium and lanthanum ions, making it clearly visible on a radiograph.[3,31,85]

Glass ionomer cement can adhere to several different types of material including: composite resin, amalgam and other metals.[54,72,75]

1.7 Disadvantages of Glass Ionomer cements

Most conventional glass ionomer cements still show low fracture toughness and wear resistance compared to other restorative materials such as amalgam and resin composite.[75,84,86] The fracture toughness and wear resistance is dependent on factors such as: the composition of the glass; the type and concentration of the polyalkenoic acid; the size of the glass powder particles[85]; the relative proportions of the glass/polyalkenoic acid/tartaric acid/water constituents and the mixing process.[75] These same factors also have an influence on the working and setting characteristics of this material.[75,85]

There have been advanced improvements in the glass ionomers available on the market today, giving them superior physical properties compared to traditional glass ionomers. Modern glass ionomers have a high viscosity related to the high cross-linkage formed in the matrix, made possible by optimization of the polyalkenoic acid and particle size distribution.[82,84] Some of the modern glass ionomers have a special nano-filled coating to increase the wear resistance of the material.[82,84] Research on the long-term clinical success of modern Glass Ionomers is still ongoing.[82,84,87,88]

The working time of glass ionomer cements are short as the first phase of the setting reaction occurs within two to three minutes after mixing. The initial hardening is followed by a relatively slow chemical setting process of approximately forty eight hours.[5,73]

Moisture contamination in the early stages of setting could cause the material to dissolve[5,82,86] and be more vulnerable to erosion and abrasion.[89] Glass ionomer restorations are sensitive to hydration and dehydration and most need to be protected with a product-specific coating after placement until the restoration reaches maturity.[82,86,90] Premature exposure of the material to moisture causes swelling, weakening and leaching of ions[86], while premature loss of moisture causes shrinkage and cracking.[86,89]

Conventional glass ionomer cements are generally opaque/white in colour, which is not aesthetically pleasing when compared to resin composite material.[73] However, the modern high viscosity glass ionomers now have improved aesthetics, with products like Equia Forte (GC Corporation) available in eight different shades[91] and Ketac Universal (3M ESPE) available in six different shades.[92] The availability of a variety of shades has led to the operator being able to create restorations with tooth shade-matching ability.[9,91]

1.8 Clinical application of Glass Ionomer cements

Restorative dentistry concepts have changed over the years. The current focus is on the removal of only minimal amounts of tooth structure and the placement of an adhesive restorative material that is capable of re-mineralizing the de-mineralized tooth structure.[69,93] Public demand for alternative, non-metallic aesthetic restorations has also increased.[94] Glass Ionomers have been developed for this purpose because of the chemical adherence and fluoride releasing ability of these materials.[59]

The dental applications of glass ionomers include the restoration of primary teeth[6], the temporary restoration of permanent teeth, sealing pits and fissures, linings used under metal restorations, permanent and temporary luting cements for stainless steel crowns, space maintainers, crowns, bridges, orthodontic appliances and indirect restorations and as a base or dentine substitute under composite resin (‘sandwich technique’).[6,31,72]

In recent years, using this material as a long-term sealant over an active carious lesion (ART-technique) has become increasingly popular.[6,31,72,73]

The use of glass ionomer cement restorations in the permanent dentition, mainly for Class III anterior and Class V restorations, is advocated by some researchers.[72,73]

Two modern high viscosity glass ionomer cements, Ketac Universal (3M ESPE) and Equia Forte Fill (GC Corporation), are now indicated for restricted stress-bearing Class I and restricted stress-bearing and non-stress-bearing Class II permanent restorations on permanent teeth.[9,91]

Another possible application within dentistry includes the use of glass ionomer cement as a bone substitute for augmentation of the alveolar ridge of edentulous patients according to research done by Brook.[28,95]

In medical fields other than dentistry, glass ionomers are being used for artificial ossicles in the human ear and as bone-substitute plates for craniofacial reconstruction.[28]

Chapter 2: Aim and Objective

2.1 Aim

The aim of this *in-vitro* study was to compare the performance of capsule-mixed glass ionomer restoratives with their hand-mixed equivalents in terms of compressive strength, surface hardness and porosity.

2.2 Objective

The objective of this study was to determine whether the capsule-mixed glass ionomer restorative cements are superior in performance, if one compares the compressive strength, surface hardness and porosity, to that of the hand-mixed equivalent glass ionomer restorative cements.

2.3 Null hypothesis

The null hypothesis was that there would be no difference between the hand-mixed glass ionomer and the equivalent capsule-mixed glass ionomer regarding compressive strength, surface hardness and porosity.

Chapter 3: Materials and Methods

3.1 Study design

This *in-vitro* study compared the hand-mixed product to the equivalent capsule-mixed product of four posterior selected glass ionomer cements commercially available in South Africa regarding the compressive strength, surface hardness and porosity of the products.

3.2 Study settings

- The Oral and Dental Hospital, School of Dentistry at the University of Pretoria;
- The Department of Material Sciences and Metallurgical Engineering, University of Pretoria;
- The Micro-focus X-ray radiography/tomography facility (MIXRAD) of the South African Nuclear Energy Corporation (NECSA), Pelindaba.

3.3 Research object selection

Four posterior glass ionomer dental cements that are commercially available in South-Africa, in both hand-mix and capsule-mix variants, were selected for this study. All four of these glass ionomers are indicated for: small Class I and Class V dental restorations; primary tooth restorations; core build-up; liners under composite or amalgam restorations and temporary dental restorations. According to information obtained from the manufacturers' brochure of each product, these dental cements should have similar values for compressive strength, surface hardness and wear resistance.[9,92,96]

Images of the four products are represented in Figure 3.1 as follows: a) Riva Self-cure; b) GC Fuji IX GP; c) Ketac Universal, and d) Ketac Molar. Information regarding the manufactures are specified in Table 3.1. The composition of the products are specified in Table 3.2.

Figure 3.1: The dental glass ionomer cements used in the current study a) Riva Self Cure, b) GC Fuji IX GP, c) Ketac Universal and d) Ketac Molar. The hand-mixed and capsulated constituents of each product are illustrated.

Table 3.1: Material abbreviations, manufacturers' details and batch numbers

Material	Material Abbreviation	Manufacturer	Batch Number
Riva Self Cure hand-mix	RSCH	SDI Limited, Victoria, Australia.	114500V
Riva Self Cure capsule-mix	RSCC	SDI Limited, Victoria, Australia.	B1609013F
Riva Coat	RC	SDI Limited, Victoria, Australia.	160821
GC Fuji IX GP hand-mix	FIXH	GC Europe N.V., Leuven, Belgium.	1706261
GC Fuji IX GP capsule-mix	FIXC	GC Europe N.V., Leuven, Belgium.	170810A
GC Fuji Coat LC	FIXCLC	GC Europe N.V., Leuven, Belgium.	1705151
Ketac Universal hand-mix	KUH	3M ESPE, Seefeld, Germany.	Powder 3419910 Liquid 634377
Ketac Unversal Aplicap capsule-mix	KUC	3M ESPE, Seefeld, Germany.	3550324
Ketac Molar Easymix hand-mix	KMH	3M ESPE, Seefeld, Germany.	Powder 667574 Liquid 651646
Ketac Molar Aplicap capsule-mix	KMC	3M ESPE, Seefeld, Germany.	3302403

Table 3.2: Material composition and manufacturer powder/liquid ratio recommendation

Material	Composition	Manufacturer recommended powder/liquid ratio
Riva Self Cure hand-mix	Fluoro-alumino-silicate glass, polyacrylic acid + tartaric acid, water	3.3:1
Riva Self Cure capsule-mix	Fluoro-alumino-silicate glass, polyacrylic acid + tartaric acid, water	3.2:1
GC Fuji IX GP hand-mix	Alumino-fluoro-silicate glass, polyacrylic acid, distilled water, polybasic carboxylic acid	3.6:1
GC Fuji IX GP capsule-mix	Alumino-fluoro-silicate glass, polyacrylic acid, distilled water, polybasic carboxylic acid	3.5:1
Ketac Universal hand-mix	Oxide glass powder, acrylic acid-maleic acid copolymer, water, tartaric acid, benzoic acid	3:1
Ketac Universal Aplicap capsule-mix	Oxide glass powder, acrylic acid-maleic acid copolymer, water, tartaric acid, benzoic acid	3.2:1
Ketac Molar Easymix hand-mix	Aluminium-calcium-lanthanum-fluoro-silicate glass powder, polyacrylic acid, acrylic acid-maleic acid copolymer, water, tartaric acid	4.5:1
Ketac Molar Aplicap capsule-mix	Aluminium-calcium-lanthanum-fluoro-silicate glass powder, polyacrylic acid, acrylic acid-maleic acid copolymer, water, tartaric acid	3.4:1

3.4 Measurements

The research was performed in a controlled environment that met with the manufacturers' recommendations at 23 +/- 1˚C and 50 +/- 5% relative humidity.[47,97]

Test materials were mixed and dispensed in polytetraflouroethyle (PTFE) moulds, having the following internal dimensions: six millimetres in height and four millimetres in diameter.[38,41,97,98,99] The moulds were constructed from PTFE tubing which were supported by custom-made perspex blocks as illustrated by Figure 3.2.[51] The resultant cylindrical specimens were prepared by two operators with the same level of training to simulate operator variability.[43,98]

The measuring scoops for powder and liquid dropper bottles provided for each respective product were used to measure the accurate quantities for hand-mixed materials according to manufacturer's instructions. In order to simulate clinical practice, the powder and liquid quantities for hand-mixed materials were intentionally not weighed. This decision was taken to ensure that this study would be relevant to real-life/clinical dental practice circumstances.

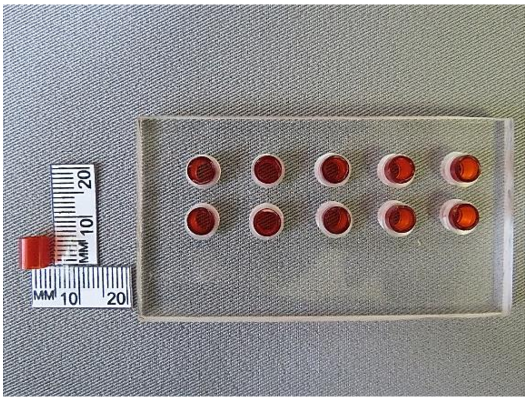

Figure 3.2: Cylindrical moulds manufactured from polytetraflouroethyle (PTFE) tubing supported in a custom-manufactured Perspex block

Forty nominally identical cylindrical hand-mixed glass ionomer specimens were manufactured for each test that was carried out. A second set of 40 nominally identical, cylindrical, capsule-mixed glass ionomer specimens were manufactured for each test that was carried out.

In summary:

Riva Self Cure

10 hand-mixed specimens + 10 capsule-mixed specimens for compressive strength testing.

10 hand-mixed specimens + 10 capsule-mixed specimens for surface hardness testing.

10 hand-mixed specimens + 10 capsule-mixed specimens for porosity testing.

GC Fuji IX GP

10 hand-mixed specimens + 10 capsule-mixed specimens for compressive strength testing.

10 hand-mixed specimens + 10 capsule-mixed specimens for surface hardness testing.

10 hand-mixed specimens + 10 capsule-mixed specimens for porosity testing.

Ketac Universal

10 hand-mixed specimens + 10 capsule-mixed specimens for compressive strength testing.

10 hand-mixed specimens + 10 capsule-mixed specimens for surface hardness testing.

10 hand-mixed specimens + 10 capsule-mixed specimens for porosity testing.

Ketac Molar

10 hand-mixed specimens + 10 capsule-mixed specimens for compressive strength testing.

10 hand-mixed specimens + 10 capsule-mixed specimens for surface hardness testing.

10 hand-mixed specimens + 10 capsule-mixed specimens for porosity testing.

Only the capsules of GC Fuji IX GP were shaken to loosen the powder before activation according to manufacturers' instructions.[100] All the capsules were activated (Figure 3.4) for two seconds (as per manufacturers' instructions) to break the membrane separating the powder and liquid components.[38,47,100] The capsules were then placed into a mechanical mixing machine immediately thereafter.

All the 3M ESPE capsules were mixed in the Rotomix^{TM} (3M ESPE, United Kingdom) (Figure 3.3), in accordance with manufacturers' instructions. The machine was set on an eight seconds vibratory action, with an additional three seconds centrifuging action at 2950 rpm frequency.[38,47,51]

The other capsules were mixed in an amalgam-mixer (Amalgamator SYG 200, SMACO, Switzerland) (Figure 3.3) in accordance with manufacturers' instructions for 10 sec of vibratory action.[38,47]

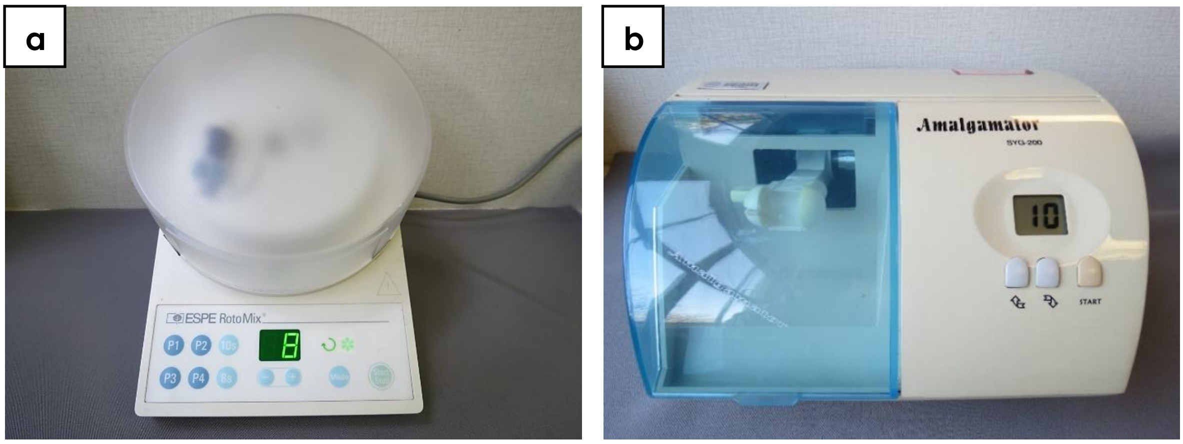

Figure 3.3: Mechanical mixing machines a) Rotomix^{TM} (3M ESPE), b) Amalgamator (SYG 200, SMACO)

Immediately after mixing, each capsule was placed in the appropriate applicator (Figure 3.4) to facilitate the extrusion of the glass ionomer restorative material.[38,47]

Figure 3.4: Capsule activator used with 3M ESPE products (top) and applicator used with all products tested (below)

The hand-mixed equivalents of the capsulated Glass Ionomer restoratives were hand-mixed according to the manufacturers' recommended powder to liquid ratio for each product on a waxed paper mixing pad (Figure 3.5) using the scoop provided and dropper system (Figure 3.1).[43]

The powder bottles of GC Fuji IX GP hand-mix and Riva Self Cure hand-mix were tapped against the hand to ensure accurate dispensing of the powder according to manufactures' recommendations.[101,102] The powder of Ketac Molar Easymix and Ketac Universal were fluffed by shaking the bottle according to the manufacturer recommendations in order to more accurately measure the scoop of powder required.[103]

The powder of each product was divided into two equal portions according to the specific manufacturer instructions.[38,101,102,103] The first portion was hand-mixed into the liquid within 10 sec with a stainless steel spatula (Figure 3.5), until fully incorporated. The second portion was then also incorporated into the liquid mixture within 20 sec.[38]

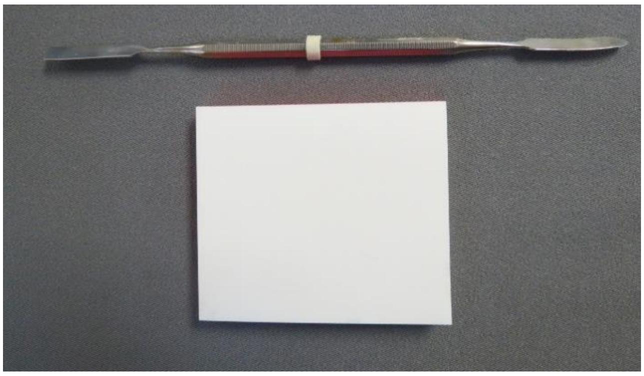

Figure 3.5: Stainless steel mixing spatula and waxed paper pad for hand-mixing

The moulds were placed on a polyester strip in the Perspex matrix. The mixed cement was dispensed into the moulds within 60 sec of mixing (Figure 3.6).[41,51,98] The mould was slightly overfilled. To minimise the incorporation of air bubbles in the set cylindrical specimens, the capsulated glass ionomers were extruded slowly from the capsule to provide laminar flow and the nozzle was positioned to one side of the mould.[38,98,104]

The hand-mixed Glass Ionomers were applied to the mould within 60 sec using a stainless steel spatula (Figure 3.5) and allowed to flow into the mould to minimise the incorporation of air bubbles.[38,41]

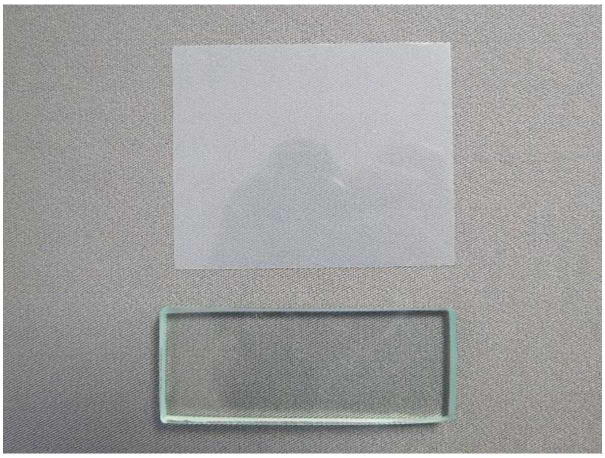

Figure 3.6: Polyester strip and glass slab

A second polyester strip was placed over the filled mould and compressed using a glass slab with a weight of 60 g (Figure 3.6 and Figure 3.7)[105] and slight pressure to extrude the excess material and flatten the surface (see Figure 3.7).[54,78,89,97,98,105,106,107,108]

Figure 3.7: Prepared specimens before coating

Either three or four minutes (depending on the manufacturer's recommendations of each test material) after the end of mixing, the specimens of Fuji IX and Riva Self-cure were covered with their respective coatings, GC Fuji Coat LC and Riva Coat (Table 3.3), as provided for each product (Figure 3.1)[89] The composition of GC Fuji Coat LC and Riva coat are specified in Table 3.3.

The coated specimens were light cured with a Valo LED curing light (Ultradent Products Inc., South Jordan, USA) (Figure 3.8) with a light-intensity of 450nm for 10 sec, also according to the manufacturers' instructions.

The specimens of the Ketac Molar "goups" were covered with petroleum jelly (Figure 3.1), according to the manufacturer's recommendations. The Ketac Universal group specimens were not covered with any coating, in line with the manufacturer's instructions.[9,92]

Table 3.3: Material coatings for GC Fuji IX GP and Riva Self Cure respectively

Varnish	Composition
GC Fuji Coat LC	Methylmethacrylate, multifunctional methacrylate, camphorquinone
Riva Coat	Acrylic monomer

Figure 3.8: Valo LED curing light, Ultradent

The specimens were then placed in distilled water in glass containers maintained at 37+/- 1°C in an incubator (Binder ED23, Tuttlingen, Germany) (Figure 3.9) for one hour.[41,51,98]

Figure 3.9: Incubator (Binder ED23)

After one hour, silicon carbide paper (880 grit) was used, under running water, to remove surplus cement at the top and bottom of the moulds.[51] Each specimen was carefully removed from it's moulds and stored in glass containers with 50 ml of distilled water at 37 °C for a further 23 hours prior to testing in order for testing to commence at 24 hours after manufacturing of the specimens.[41,55,98] Any specimens that contained defects such as visible bubbles or cracks, were discarded.[41,98]

Compressive strength

The compressive fracture strength of each specimen was determined using a Universal testing apparatus (MTS Criterion Model C45.305, MTS Systems Corporation, MN 55344-2290, U.S.A) (Figure 3.10).

The flat ends of each specimen was placed between the plates of the Universal testing apparatus with moist filter paper on either sides to prevent dehydration before commencement of testing.[109]

A gradually increasing compressive load, at a rate of at 1 mm/min to the 6 mm long axis of each specimen was enforced.[38,41,47,98,99] The tester software - MTS Testsuite (TW Elite), (Figure 3.11) was used to analyse the results. The load to fracture was recorded.

The compressive fracture strength P (MPa) was calculated using the following equation:

$$P = \frac{4F_f}{\pi d^2}$$

where F_f was the load at fracture (N), π constant for pie used as 3.14 and d the mean diameter of the specimen (mm).[38,42,98,109]

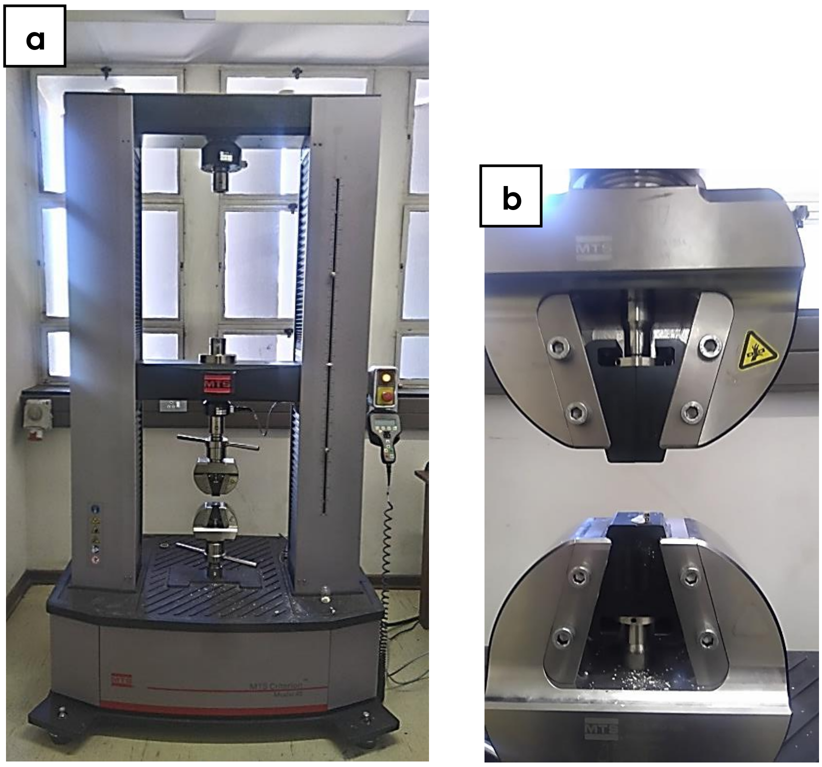

Figure 3.10: a) Universal testing apparatus (MTS Criterion Model C45.305, MTS Systems Corporation). b) Specimen placement in testing machine

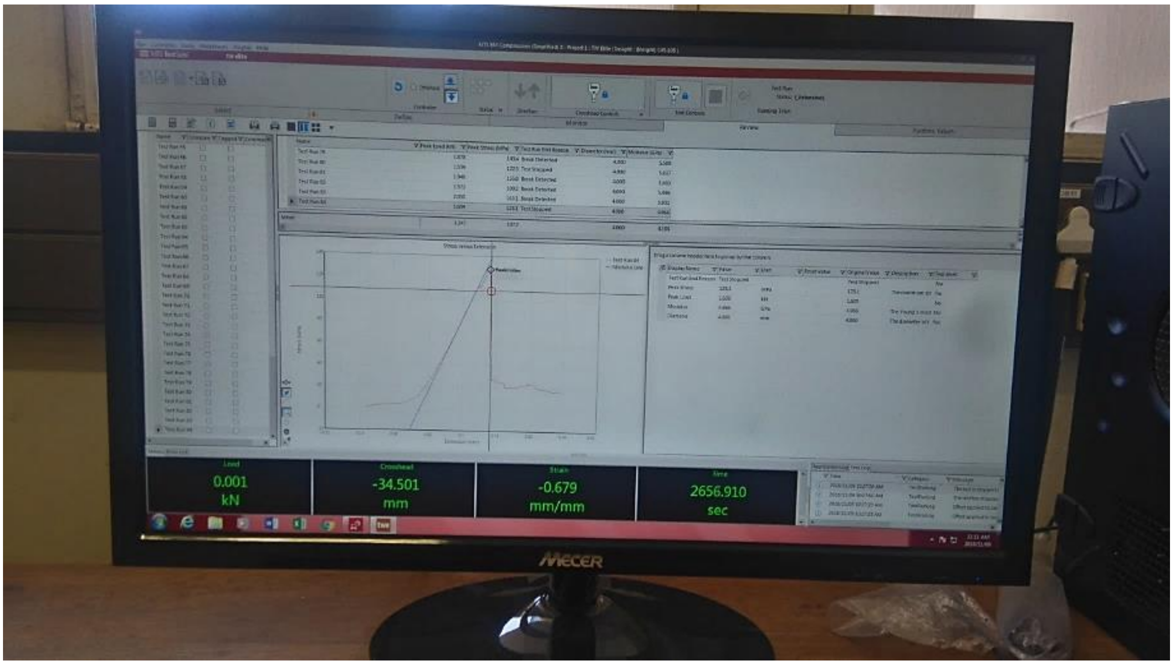

Figure 3.11: MTS Testsuite TW Elite software utilized by the Universal testing apparatus

Scanning Electron Microscope (SEM) observation

After compressive strength testing, a selection of fragments from the specimens of each product were examined within one hour by SEM (JEOL JSM IT300, JEOL Ltd., Akishima Tokyo, Japan) (Figure 3.12) with EDS Detector (Oxford X-max 50).[51] The fragments were vacuum sputter-coated with gold before SEM examination. The fragments were observed at an operating voltage of 10 kV[105], over a range of magnifications.[54] The computer made used of Oxford Aztec software (Oxford Instruments, United Kingdom) to analyse the SEM images. In the current study, SEM evaluation was done for interest sake to observe the interrelation between compressive strength and voids present in a material.

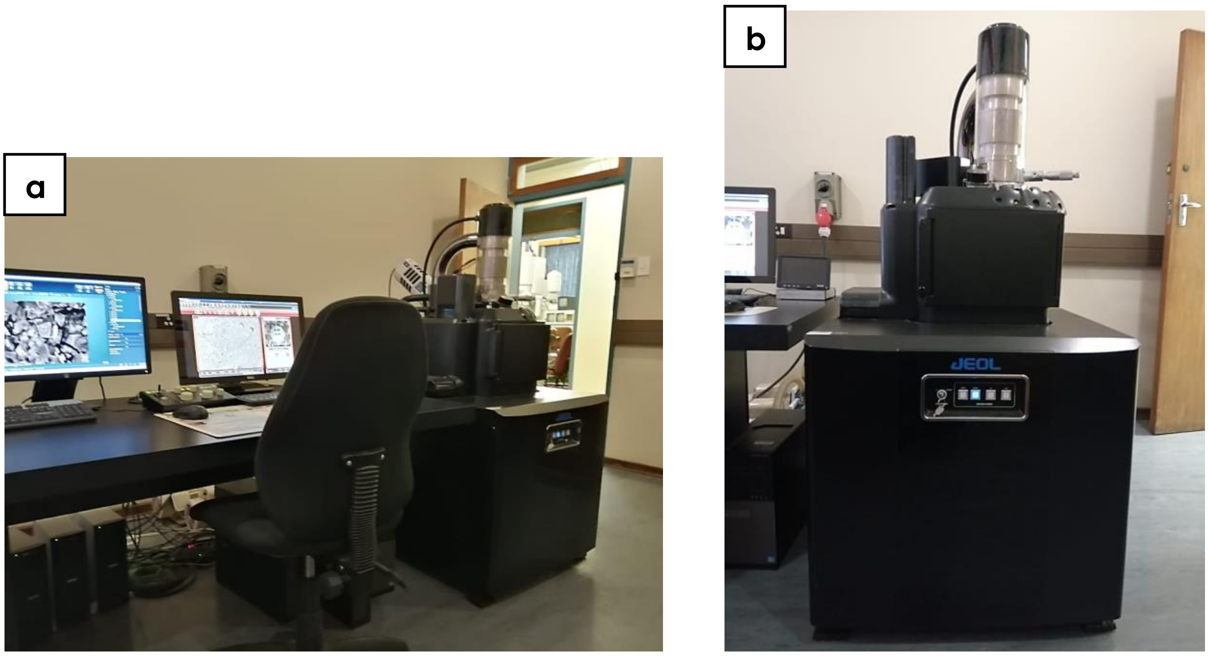

Figure 3.12: a) SEM Facility at University of Pretoria, Department of Metallurgical Engineering, b) JEOL MP-09930MAP SEM

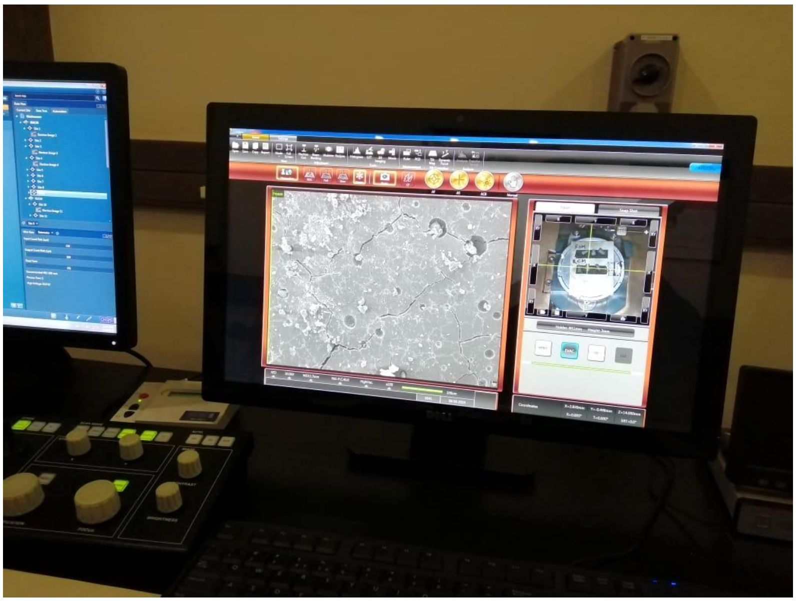

Figure 3.13: Computer with Oxford Aztec software (0xford Instruments, United Kingdom) used for analysis of the SEM images

Surface hardness

Before being subjected to Vickers hardness testing, the surfaces of each specimen was smoothed with 2500 grit silicon carbide paper, followed by 4000 grit silicon carbide paper (3M, Maplewood, MN,USA).[107,109] The carbon paper mimics the polishing of the restoration that would take place in the clinical environment.[109]

A digital micro-hardness tester with Vickers diamond indenter (Future-Tech FV 700, Kanagawa, Japan) (Figure 3.14) was used to measure the surface hardness of each glass ionomer specimen. A pyramid square diamond indenter (Vickers pyramid) with an opening angle of 136 degrees was pressed vertically into the surface of the specimens (Figure 3.15).[107]

A load of 500 mN was applied by the indenter[9,109], at five different indentation areas of each specimen[110], with a dwell time of five seconds (Figure 3.14).[107,108] The five indentations were made on one of the flat surfaces of each specimen: one in the centre and one in each quadrant, at least 1 mm from each other.[111]

The Vickers hardness number (VHN) corresponding to each indentation was calculated by the instrument after the diagonals were chosen.[109]

The five readings for each specimen were computed and the mean VHN in N/mm^2 was determined for each specimen.[108]

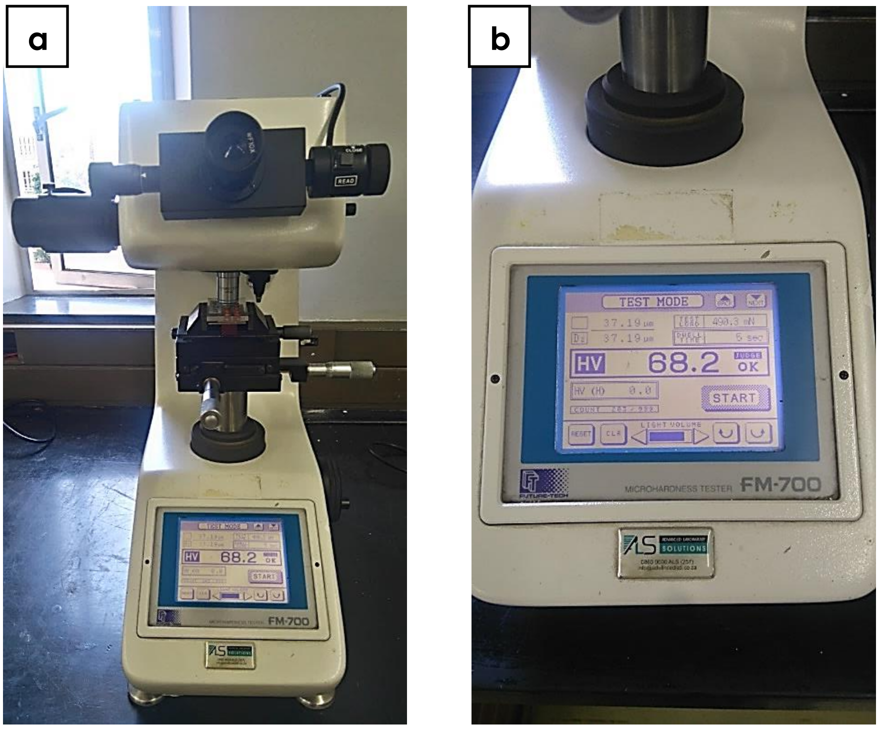

Figure 3.14: a) Digital micro-hardness tester with Vickers diamond indenter (Future-Tech FV 700) and b) close-up of the parameter and results screen of the micro-hardness tester

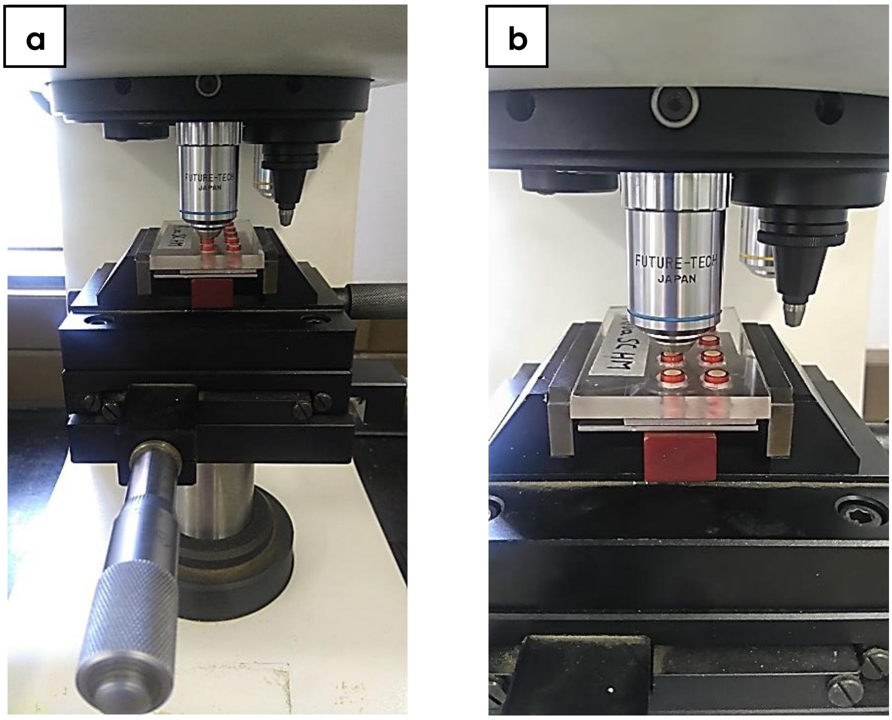

Figure 3.15: a) and b) showing the specimen position in the micro-hardness tester before load application

Porosity

The XTH 225kV micro-focus X-ray/CT system from Nikon Metrology (Leuven, Belgium) (Figure 3.16) situated at the micro-focus X-ray radiography/tomography facility (MIXRAD) of the South African Nuclear Energy Corporation (NECSA) was used for porosity testing.

The four functional units of the system consist of a lead-lined cabinet containing an X-ray tube, a sample manipulator, a flat panel detector, an external chiller, an external control module, and computers with software for the recovery and three dimensional (3D) reconstruction of images.

Figure 3.16: XTH 225 ST micro-focus X-ray tomography system (Nikon) at the MIXRAD facility (Photo courtesy of Hoffman et al.[112])

This type of system has an intrinsic 0.001- 0.006 mm spatial resolution volume.[113] The sample manipulator of the system guarantees stability of samples weighing up to 50 kg.[112] The manipulator can be altered to allow for horizontal optimization to ensure maximum amplification of the sample.[112] This alteration ensures that samples are horizontally included in two dimensional (2D) radiographs at all angles of rotation and for correct normalisation during the tomography reconstruction procedure.[112,113]

The sample manipulator can move 300 mm in the vertical plane, 200 mm in the horizontal plane and 610 mm in the beam direction which allows for a high geometrical amplification, determined by the size of the sample.[112] The rotational movement is highly accurate up to 1/1000th of a degree and thus up to 4000 or more projections in 360 degrees are possible (Figure 3.17).[113] The quantity of projections affect the resolution of the final scan.[112]

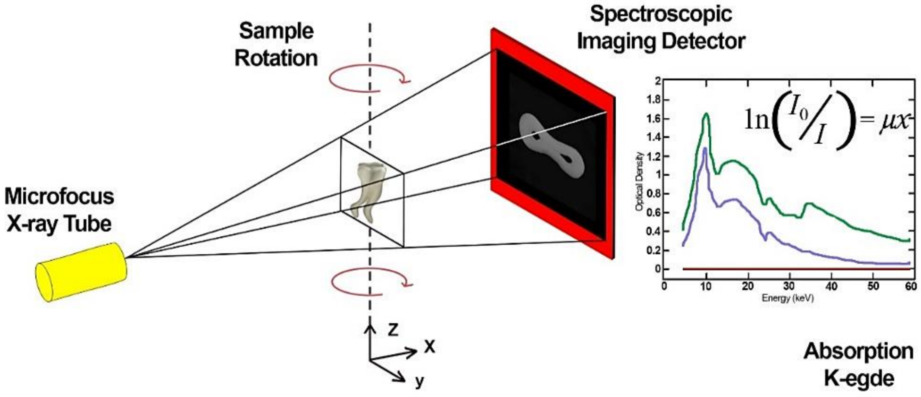

Figure 3.17: Tomographic process of the XTH 225 ST micro-focus X-ray tomography system (Nikon)

In order to convert 2D projections into 3D volume, CT-Pro reconstruction software (Nikon XT software, U.S.A) was used. The CT-Pro 3D raw volume file was then imported into VGStudioMax software (High-End Industrial CT Software, Heidelberg, Germany) which allows for the recovery of the X-rays, the reconstruction of the X-rays into a pinpoint sharp 3D virtual image, making visualization and analysis of the images possible.[112,113] The system can be adapted to characterize samples of different size, material and weight.[112] The assessment of internal surfaces, material densities and other valuable material characteristics are made possible. It can also determine the volumetric fraction and size distribution for any specific specimen.[112]

In this study the number of voids per volume (mm^3)of each specimen, the total volume of voids (mm^3) per volume of each specimen and the volume percentage of voids per volume of each specimen were determined using this system and software.[53] The measured volume of each specimen was set at 60,054688 mm^3 by the system and software. Voids greater than 0.001 mm^3 were included in this study as they are considered as significantly large voids.[53]

3.4 Ethical considerations

Approval was obtained from the University of Pretoria's Faculty of Health Sciences, Research Ethics Committee. The Helsinki Declaration was signed.

3.5 Statistical considerations

3.5.1 Sample size

No formal sample size estimation was done because this was an exploratory study, the first of it's kind in the University of Pretoria, School of Dentistry.

The statistician recommended a nominal sample size of 10 specimens per product for each of the four capsule-mixed glass ionomer restorative cements, and ten specimens per product for each of the four hand-mixed glass ionomer restorative cements, for each test to be done. The total sample size was thus 80 specimens for each of the three tests carried out as follows:

80 specimens for compressive strength testing.
80 specimens for surface hardness testing.
80 specimens for porosity testing.

The total number of specimens used for the current study was thus 240.

3.5.2 Data capturing

Values for each test performed were recorded on an MS Excel document designed specifically for the purpose of the present study.

Data were collected and combined by the researcher and the resulting datasets were confirmed by the supervisor. Thereafter, these datasets were submitted to a statistician for analysis.

3.5.3 Statistical analysis

All statistical procedures were performed on SAS (SAS Institute Inc, Carey, NC, USA), release 9.4, running under Microsoft windows for personal computer. Statistical tests were two-sided and *P* values <0.05 were considered significant.

The Shapiro-Wilk test was used to examine the normality of numerical data.

Mean values of the compressive strength, the surface hardness and the porosity were compared between the hand-mixed glass ionomer cements and equivalent capsule-mixed glass ionomer cements using the two-sample t-test to determine whether the differences between the means were random or significant.

In addition, the non-parametric Wilcoxon rank sum test was performed to compare the median values of the paired groups and test the null hypothesis that there would be no difference between the hand-mixed glass ionomer and the equivalent capsule-mixed glass ionomer regarding compressive strength, surface hardness and porosity.

Chapter 4: Results

The datasets were statistically analysed with the significance level set at P<0.05. Numerical data were examined for normality by evaluating the data distribution and using the Shapiro-Wilk test. Despite there being a few exceptions, which were determined to be chance outcomes, the data showed normal distribution.

4.1 Compressive strength

The values recorded for the load to fracture for both RSCH- and RSCC- paired groups were statistically compared. The difference between the means of each of the two groups was 24.04, which was statistically significant (p=0.027). The medians of the two groups differed by 21.35, which was also statistically significant (p=0.045).

Table 4.1 provides a summary of the statistical analysis. Figure 4.1 graphically illustrates the mean compressive strength values for RSCH and RSCC with specimens arranged in numerical order from smallest to largest values.

Table 4.1: Statistical comparison of the compressive strength values of RSCH and RSCC

	RSCH	**RSCC**	**p Value**
n	10	10	
Mean (+- SD)	86.820 (24.371)	110.86 (20.097)	0.027*
Median (IQR)	88.350 (63.40-107.70)	109.70 (92.70-125.60)	0.045**
Min/Max	41.40/114.70	85.20/149.40	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

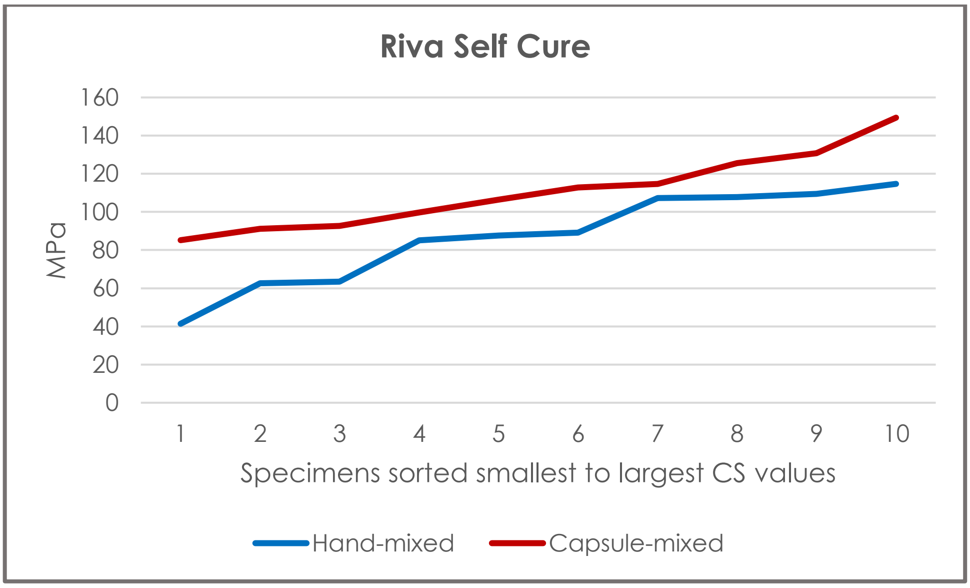

Figure 4.1: Compressive strength mean values (MPa) for RSCH and RSCC specimens arranged in numerical order from smallest to largest values

The difference between the means of the data obtained from the load to fracture values for FIXH- and FIXC- paired groups was 9.69, which was not statistically significant (p=0.254). The difference between the medians of these same two groups was 2.45, which was also not statistically significant (p=0.364). Table 4.2 provides a summary of the statistical analysis. Figure 4.2 displays the mean compressive strength values for FIXH and FIXC with specimens arranged in numerical order from smallest to largest values.

Table 4.2: Statistical comparison of the compressive strength values of FIXH and FIXC

	FIXH	FIXC	p Value
n	10	10	
Mean (+- SD)	102.950 (22.245)	112.640 (13.502)	0.254*
Median (IQR)	106.10 (89.40-121.50)	108.550 (101.70-126.50)	0.364**
Min/Max	55.40/127.50	96.80/132.90	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

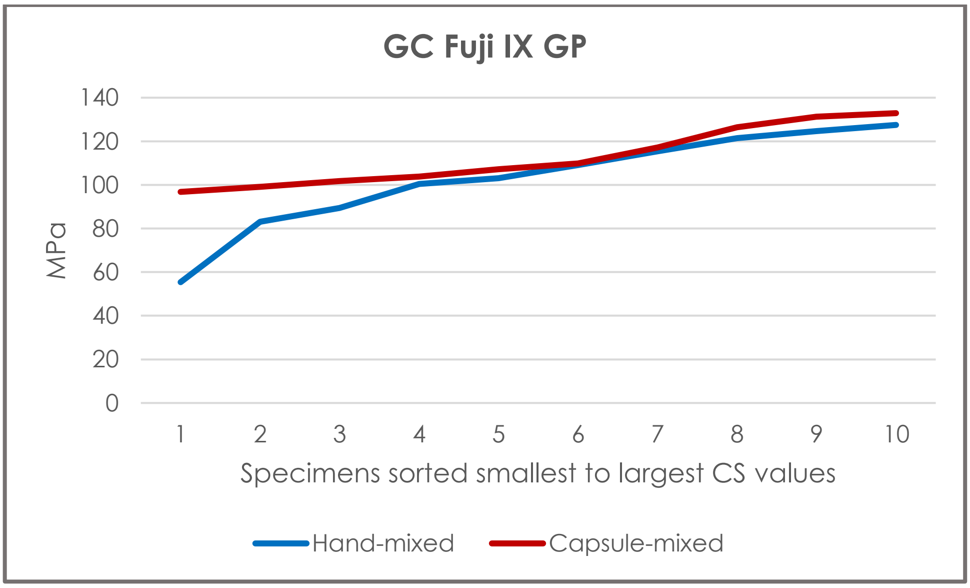

Figure 4.2: Compressive strength mean values (MPa) for FIXH and FIXC specimens arranged in numerical order from smallest to largest values

The statistical comparison of the load to fracture data for KUH and KUC paired groups revealed a difference of 14.96 when the means for the two groups were compared, which was not statistically significant (p=0.090). The medians for the data of these two groups differed by 8.995, which was also not statistically significant (p=0.131).

Table 4.3 provides a summary of the statistical analysis. Figure 4.3 graphically represents the mean compressive strength values for KUH and KUC with specimens arranged in numerical order from smallest to largest values.

Table 4.3: Statistical comparison of the compressive strength values of KUH and KUC

	KUH	KUC	p Value
n	10	10	
Mean (+- SD)	110.20 (20.074)	125.160 (17.174)	0.090*
Median (IQR)	112.705 (100.90-122.70)	121.70 (115.20-144.10)	0.131**
Min/Max	78.50/145.40	100.30/153.0	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

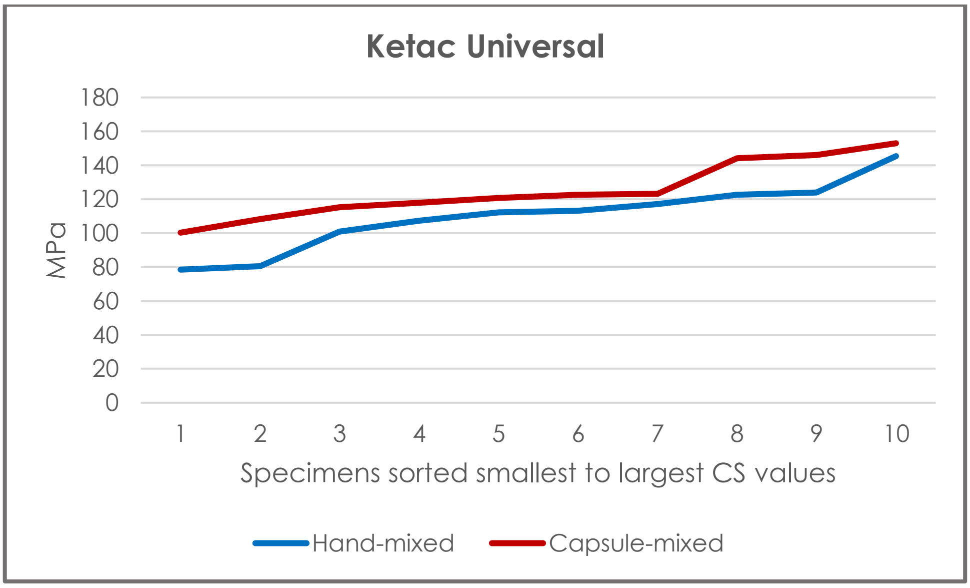

Figure 4.3: Compressive strength mean values (MPa) for KUH and KUC specimens arranged in numerical order from smallest to largest values

When the load to fracture statistical data for KMH and KMC paired groups were investigated, the means for the two groups differed by 49.11, which was statistically significant (p<0.001). The medians for the two groups differed by 56, which was also statistically significant (p<0.001).

Table 4.4 provides a summary of the statistical analysis. Figure 4.4 graphically depicts the mean compressive strength values for KMH and KMC with specimens arranged in numerical order from smallest to largest values.

Table 4.4: Statistical comparison of the compressive strength values of KMH and KMC

	KMH	**KMC**	**p Value**
n	10	10	
Mean (+- SD)	89.630 (13.602)	138.740 (18.362)	<0.001*
Median (IQR)	85.30 (81.10-92.50)	141.30 (122.50-155.0)	<0.001**
Min/Max	72.80/115.20	109.20/163.10	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

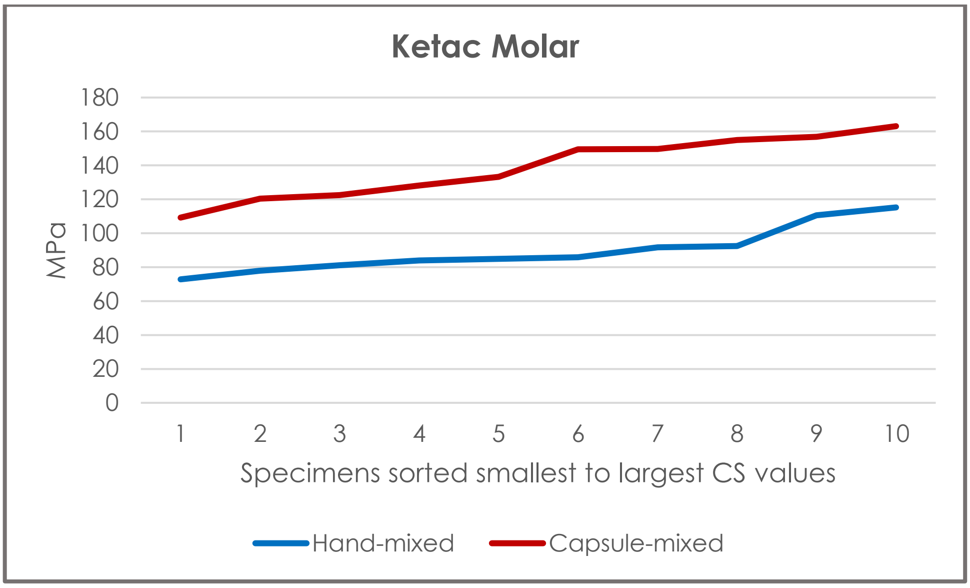

Figure 4.4: Compressive strength mean values (MPa) for KMH and KMC specimens arranged in numerical order from smallest to largest values

4.1.1 Scanning Electron Microscope analysis

The SEM images selected for the current study are not all at the same magnification. It is not possible to accurately compare crack sizes and void depths/sizes between products using these images. A follow-up study specifically aimed at SEM image comparisons at the same magnifications would be an interesting and useful addition to the current study.

Figure 4.5 represent SEM images of fragmented surfaces of RSCH at 180 and 220 magnification. Visual observation of the images shows a high degree of porosity on the surface with cracks running between the voids.

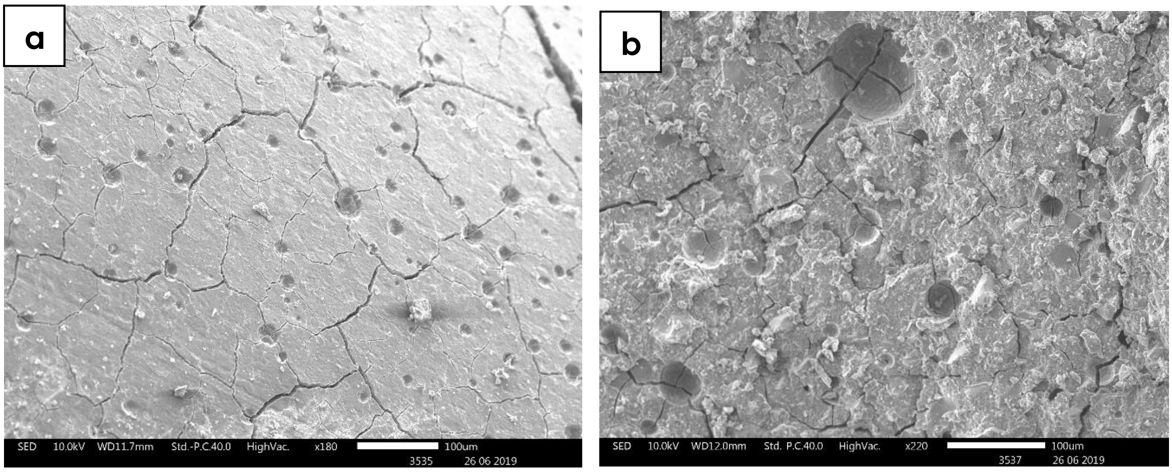

Figure 4.5: SEM images of RSCH at a) X 180 magnification and b) X 220 magnification

Figure 4.6 represents SEM images of fragmented surfaces of RSCC at X 220 and X 600 magnification. Visual observation suggest that the void density is less when compared to RSCH, with fracture lines connecting the voids.

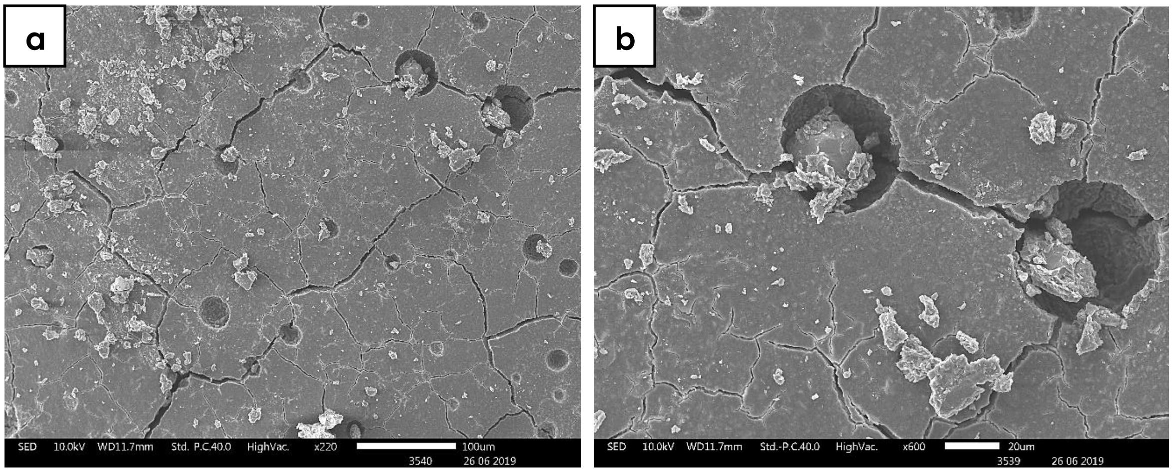

Figure 4.6: SEM images of RSCC at a) X 220 magnification and b) X 600 magnification

Figure 4.7 represents SEM images of fragmented surfaces of FIXH at X 270 and X 600 magnification. Visual observation of the images show a high void density. Fracture lines are evident between voids, but the fracture lines seem to be shallower and narrower.

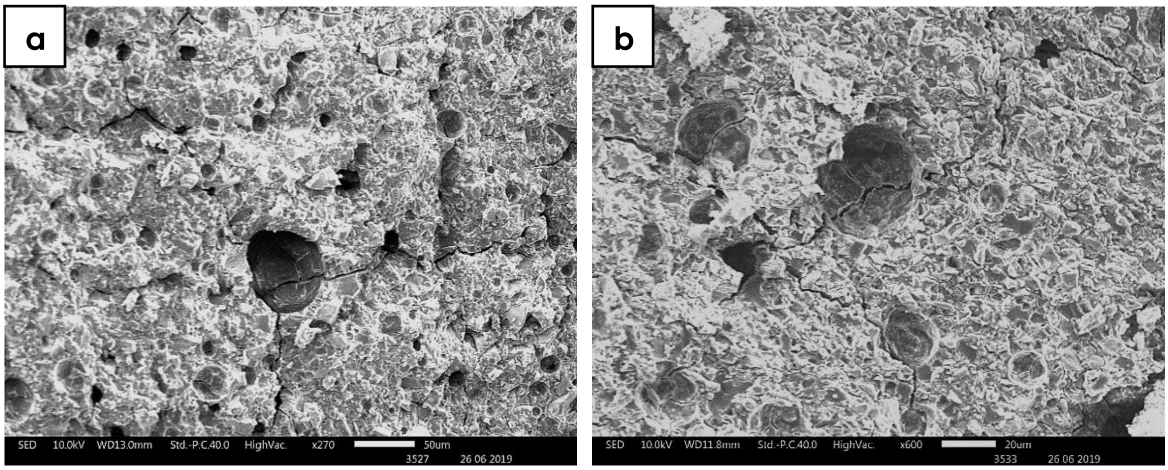

Figure 4.7: SEM images of FIXH at a) X 270 magnification and b) X 600 magnification

Figure 4.8 displays SEM images of fragmented surfaces of FIXC at X 100 and X 400 magnification. Large voids with a high density of small voids are evident when visual inspection is performed. Cracks running between voids seem to be much less prominent and much more shallow when compared to FIXH.

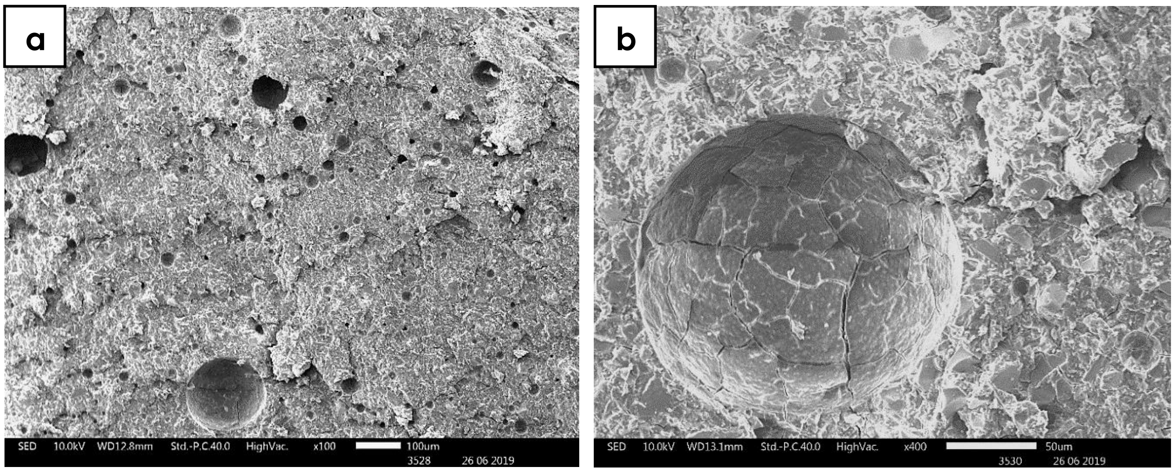

Figure 4.8: SEM images of FIXC at a) X 100 magnification and b) X 400 magnification

Figure 4.9 portrays SEM images of fragmented surfaces of KUH at X 95 and X 170 magnification. Large, deep voids are present with a low density of smaller voids on visual inspection. Fine cracks run between larger voids.

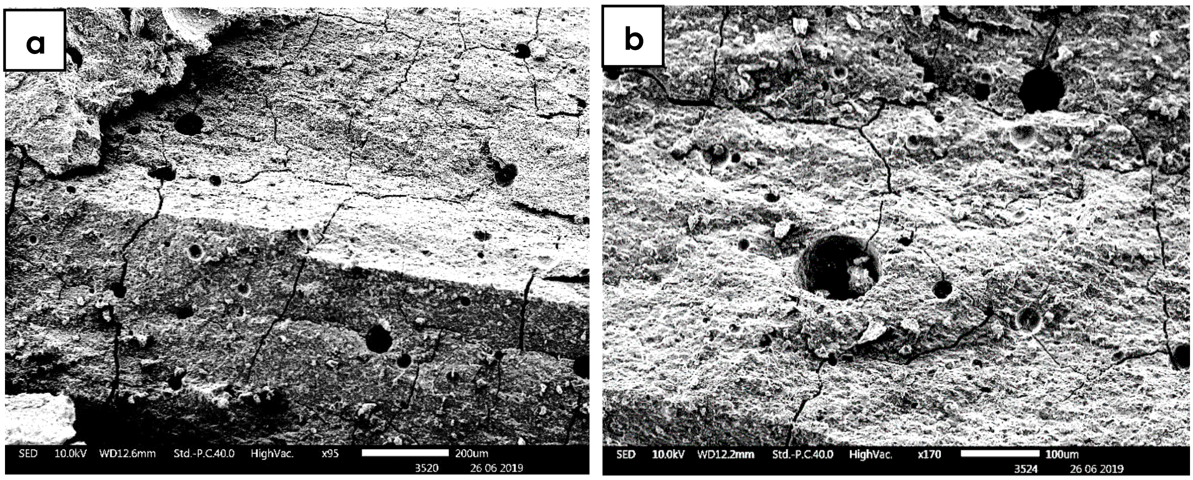

Figure 4.9: SEM images of KUH at a) X 95 magnification and b) X 170 magnification

Figure 4.10 displays SEM images of fragmented surfaces of KUC at X 220 and X 600 magnification. Visual examination shows large voids and small voids. The voids seem shallower when compared with voids in KUH. Fine fracture lines run between voids.

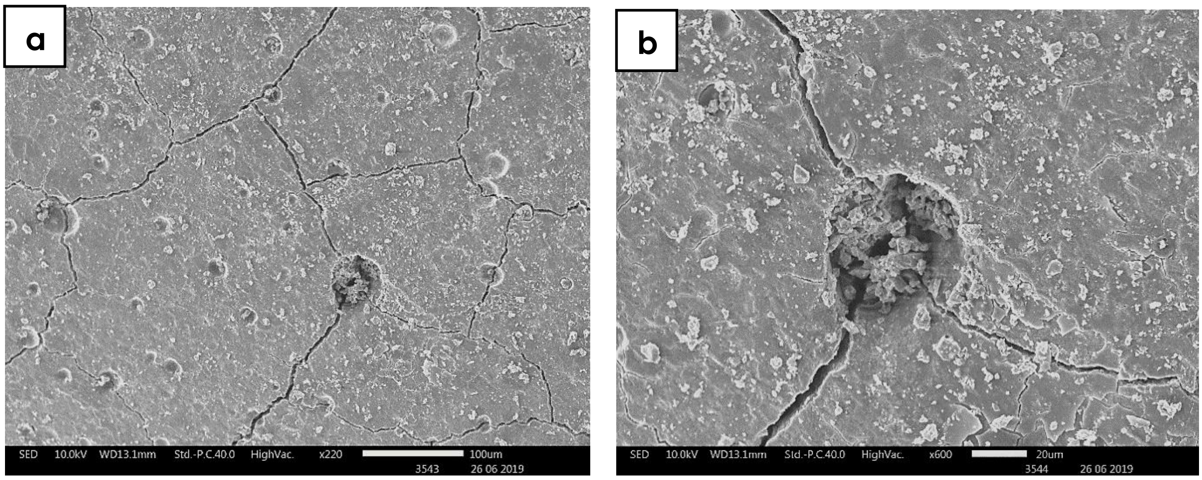

Figure 4.10: SEM images of KUC at a) X 220 magnification and b) X 600 magnification

Figure 4.11 depicts SEM images of fragmented surfaces of KMH at X 270 and X 650 magnification. Visual observation shows a rough surface texture with a high density of voids. Voids appear to be deep. Fracture lines are more promenent between larger voids.

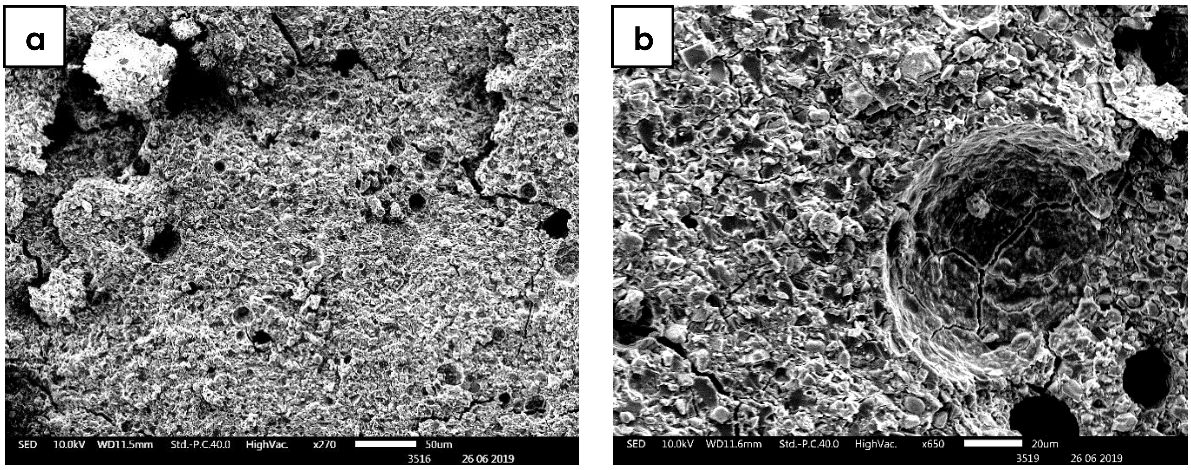

Figure 4.11: SEM images of KMH at a) X 270 magnification and b) X 650 magnification

Figure 4.12 represents SEM images of fragmented surfaces of KMC at X 220 and X 600 magnification. The surface texture seems to be smoother and more homogeneous when compared to KMH on visual inspection. Voids are shallower and the density appear to be less when compared to KMH. Fine fracture lines progress between larger and smaller voids.

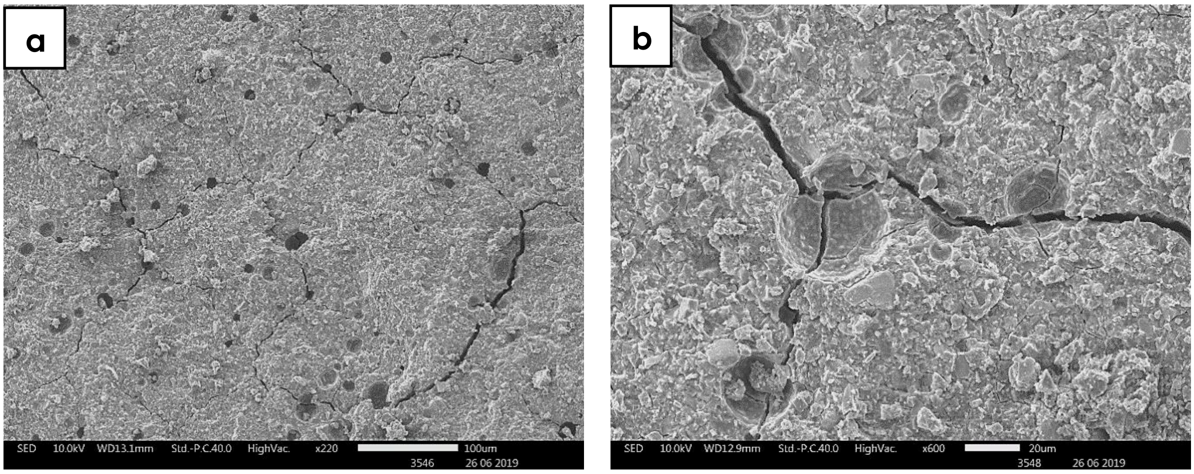

Figure 4.12: SEM images of KMC at a) X 220 magnification and b) X 600 magnification

4.2 Surface hardness

The surface hardness statistical data for RSCH- and RSCC- paired groups were examined, and presented with a difference of 6.28 in mean values for the two groups, which was not statistically significant (p=0.124). The median values for the two groups differed by 0.69, which was also not statistically significant (p=0.290).

Table 4.5 provides a summary of the statistical analysis. Figure 4.13 graphically shows the mean surface hardness values for RSCH and RSCC with specimens arranged in numerical order from smallest to largest values.

Table 4.5: Statistical comparison of the surface hardness values of RSCH and RSCC

	RSCH	RSCC	p Value
n	10	10	
Mean (+- SD)	53.350 (8.390)	59.630 (8.990)	0.124*
Median (IQR)	56.250 (47.860-58.860)	56.940 (53.440-67.20)	0.290**
Min/Max	38.660/63.480	46.480/75.80	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

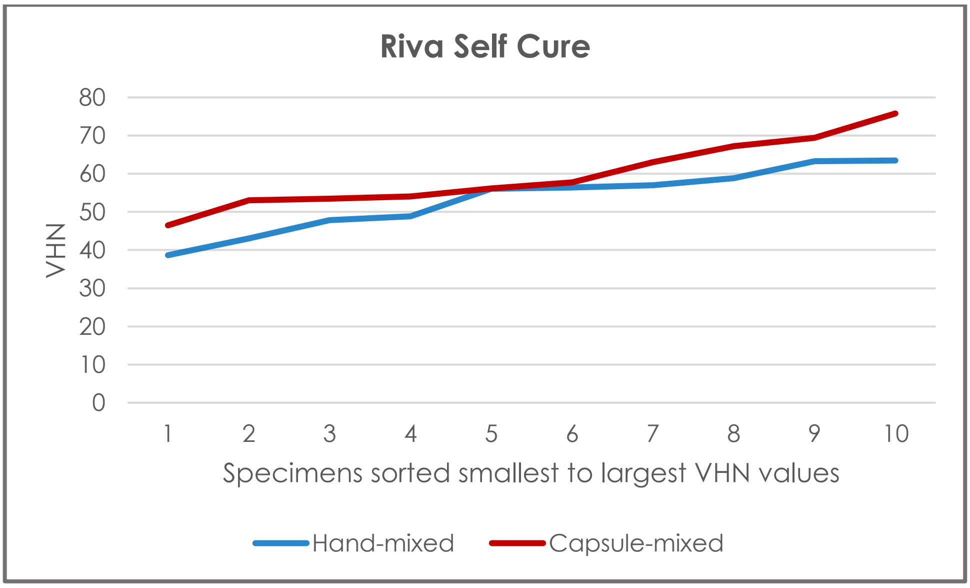

Figure 4.13: Surface hardness mean values (VHN) for RSCH and RSCC specimens arranged in numerical order from smallest to largest values

The surface hardness statistical data for FIXH- and FIXC- paired groups exhibited a difference of 11.55 in means values for the two groups, which was statistically significant (p=0.031). In addition, the medians for the two groups differed by 15.36, which was also statistically significant (p=0.034).

Table 4.6 provides a summary of the statistical analysis. Figure 4.14 graphically depicts the mean surface hardness values for FIXH and FIXC with specimens arranged in numerical order from smallest to largest values.

Table 4.6: Statistical comparison of the surface hardness value of FIXH and FIXC

	FIXH	FIXC	p Value
n	10	10	
Mean (+- SD)	61.210 (8.790)	72.760 (12.880)	0.031*
Median (IQR)	56.890 (53.940-68.980)	72.250 (64.20-79.340)	0.034**
Min/Max	52.380/74.720	55.020/93.30	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

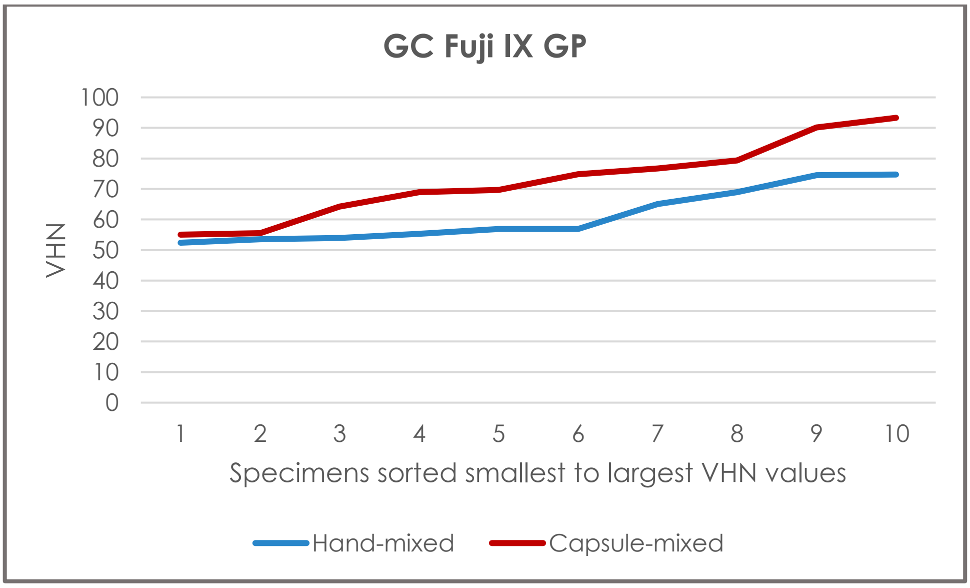

Figure 4.14: Surface hardness mean values (VHN) for FIXH and FIXC specimens arranged in numerical order from smallest to largest values

The surface hardness data for KUH- and KUC- paired groups were examined. The means for the two groups differed by 43.96, which was statistically significant ($p<0.001$). The medians for the two groups differed by 47.03, which was statistically significant ($p<0.001$).

Table 4.7 provides a summary of the statistical analysis. Figure 4.15 graphically represents the mean surface hardness values for KUH and KUC with specimens arranged in numerical order from smallest to largest values.

Table 4.7: Statistical comparison of surface hardness values of KUH and KUC

	KUH	KUC	p Value
n	10	10	
Mean (+- SD)	53.390 (20.720)	97.350 (11.070)	<0.001*
Median (IQR)	53.620 (34.860-72.240)	100.650 (83.920-104.760)	<0.001**
Min/Max	28.660/89.540	81.220/112.80	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

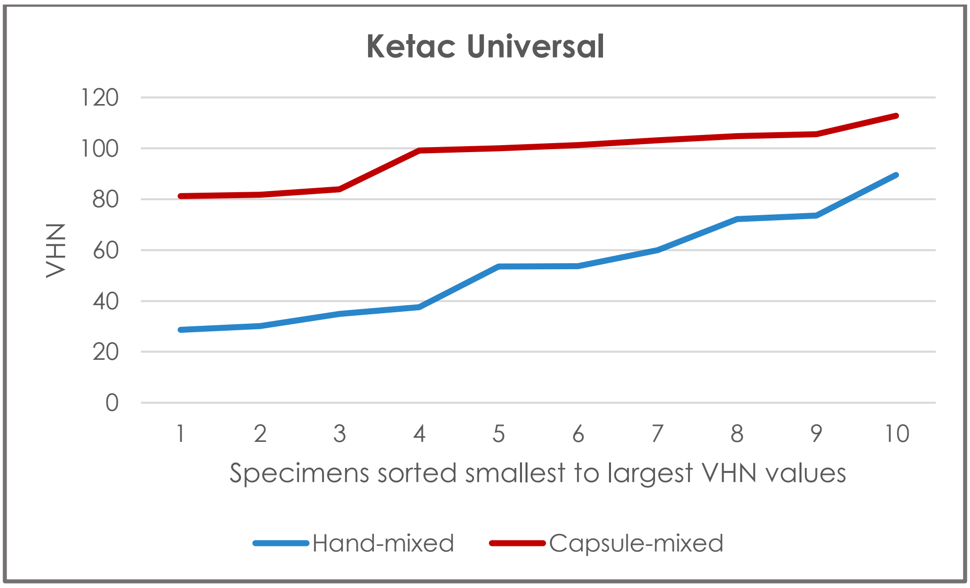

Figure 4.15: Surface hardness mean values (VHN) for KUH and KUC specimens arranged in numerical order from smallest to largest values

The surface hardness statistical data for KMH- and KMC- paired groups were compared and presented with mean values that differed by 12.95, which was statistically significant (p=0.006). The medians for the two groups differed by 18.54, which was also statistically significant (p=0.019).

Table 4.8 provides a summary of the statistical analysis. Figure 4.16 graphically displays the mean surface hardness values for KMH and KMC with specimens arranged in numerical order from smallest to largest values.

Table 4.8: Statistical comparison of the surface hardness values of KMH and KMC

	KMH	KMC	p Value
n	10	10	
Mean (+- SD)	60.790 (9.840)	73.740 (8.840)	0.006*
Median (IQR)	57.10 (54.560-69.580)	75.640 (68.060-79.080)	0.019**
Min/Max	48.260/79.440	54.980/85.260	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

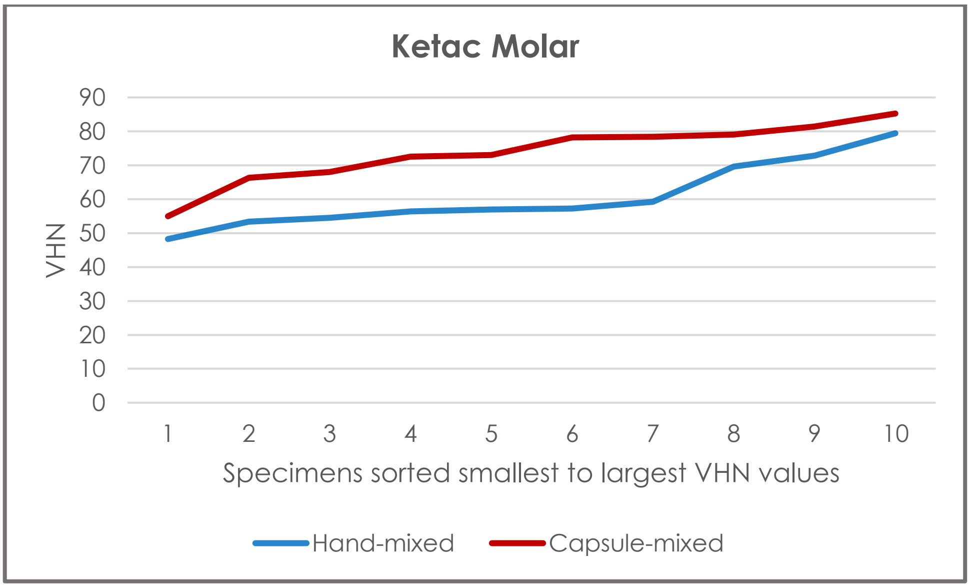

Figure 4.16: Surface hardness mean values (VHN) for KMH and KMC specimens arranged in numerical order from smallest to largest values

4.3 Porosity

Number of voids

The statistical data comparing the number of voids present in RSCH- and RSCC-paired groups were analysed and exhibited mean values that differed by 5791.5, which was not statistically significant (p=0.221). Additionally, the median values of the two groups differed by 6702, which was also not significant (p=0.199). Table 4.9 provides a summary of the statistical analysis. Figure 4.17 graphically displays the mean values for the number of voids in RSCH and RSCC with specimens arranged in numerical order from smallest to largest values.

Table 4.9: Statistical comparison of the number of voids values of RSCH and RSCC

	RSCH	RSCC	p Value
n	10	10	
Mean (+- SD)	37944.20 (12566.680)	32152.70 (7126.771)	0.221*
Median (IQR)	38217.0 (25651.0-42226.0)	31515.0 (29779.0-35645.0)	0.199**
Min/Max	24102.0/66510.0	21066.0/47681.0	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

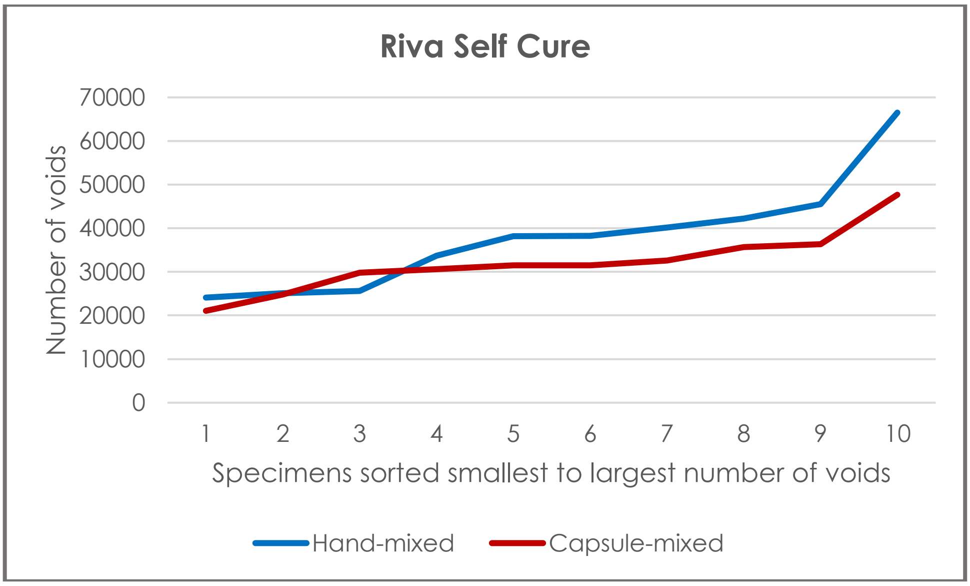

Figure 4.17: Mean values for the number of voids in RSCH and RSCC specimens arranged in numerical order from smallest to largest values

The statistical data collating the number of voids present in FIXH- and FIXC-paired groups was examined. The mean values differed by 6556.2, which was not statistically significant (p=0.210). The median values of the two groups differed by 5750.5, which was also not significant (p=0.545).

Table 4.10 provides a summary of the statistical analysis. Figure 4.18 graphically depicts the mean values for the number of voids in FIXH and FIXC with specimens arranged in numerical order from smallest to largest values.

Table 4.10: Statistical comparison of the number of voids values of FIXH and FIXC

	FIXH	FIXC	p Value
n	10	10	
Mean (+- SD)	50495.60 (14080.397)	43939.40 (7458.550)	0.210*
Median (IQR)	51705.0 (37386.0-60995.0)	45954.50 (40243.0-48670.0)	0.545**
Min/Max	31696.0/71905.0	25813.0/50851.0	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

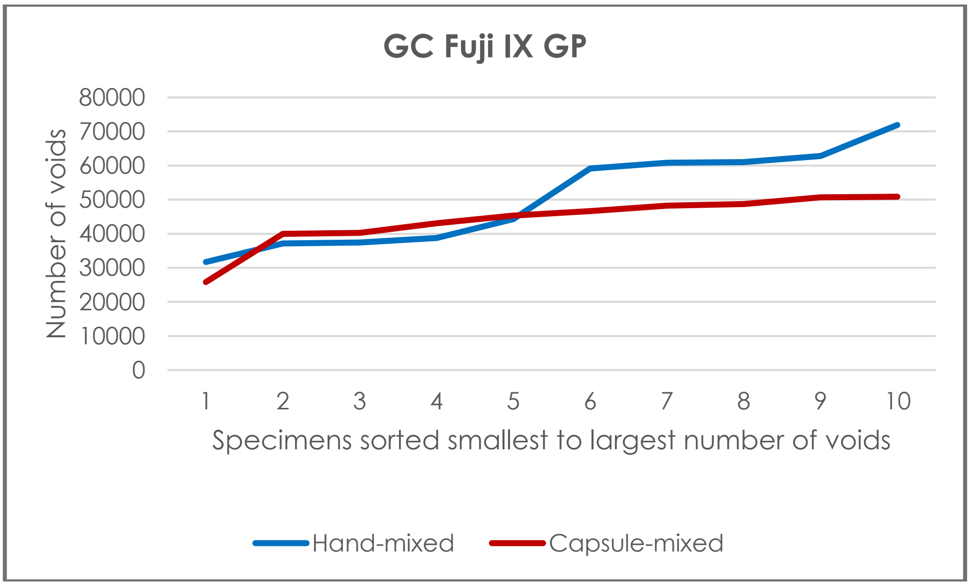

Figure 4.18: Mean values for the number of voids in FIXH and FIXC specimens arranged in numerical order from smallest to largest values

The statistical data collating the number of voids present in KUH- and KUC-paired groups was examined. The mean values varied by 12183.6, which was statistically significant (p<0.001). The median values of the two groups varied by 13694, which was also significant (p=0.002).

Table 4.11 provides a summary of the statistical analysis. Figure 4.19 graphically represents the mean values for the number of voids in KUH and KUC with specimens arranged in numerical order from smallest to largest values.

Table 4.11: Statistical comparison of the number of voids values of KUH and KUC

	KUH	KUC	p Value
n	10	10	
Mean (+- SD)	22305.60 (2825.054)	10122.0 (6314.827)	<0.001*
Median (IQR)	21794.0 (20489-23203)	8100.0 (6939-10270)	0.002**
Min/Max	18679.0/28917.0	5709.0/27469.0	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

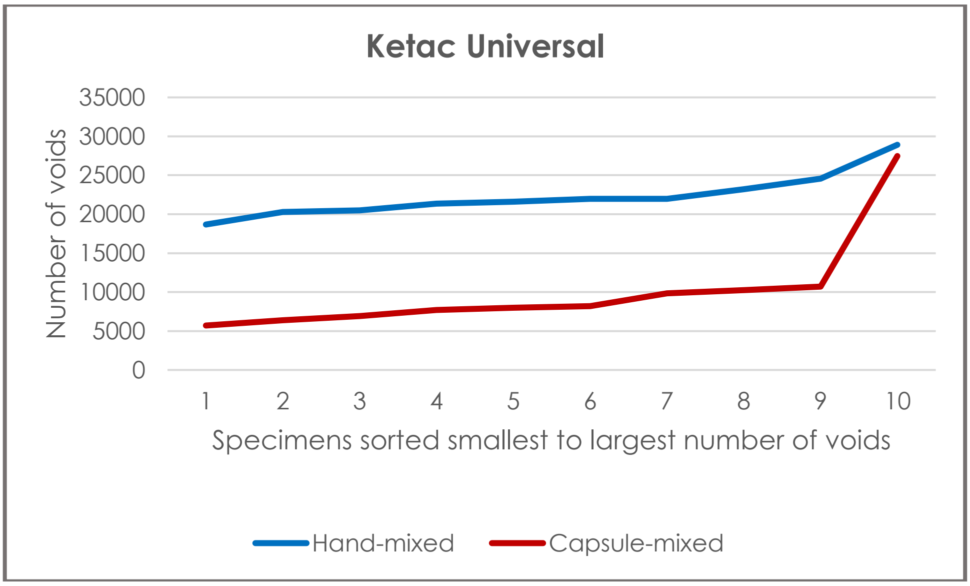

Figure 4.19: Mean values for the number of voids in KUH and KUC specimens arranged in numerical order from smallest to largest values

The number of voids statistical data of KMH- and KMC- paired groups was examined. The mean values varied by 6699.8, which was statistically significant (p=0.001). The median values of the two groups varied by 6666.5, which was also significant (p=0.007).

Table 4.12 provides a summary of the statistical analysis. Figure 4.20 graphically displays the mean values for the number of voids in KMH and KMC with specimens arranged in numerical order from smallest to largest values.

Table 4.12: Statistical comparison of KMH and KMC number of voids values

	KMH	KMC	p Value
n	10	10	
Mean (+- SD)	16306.50 (4542.120)	9606.70 (2230.991)	0.001*
Median (IQR)	17075.0 (15107.0-19669.0)	10408.50 (7259.0-11102.0)	0.007**
Min/Max	8249.0/22674.0	6073.0/12105.0	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

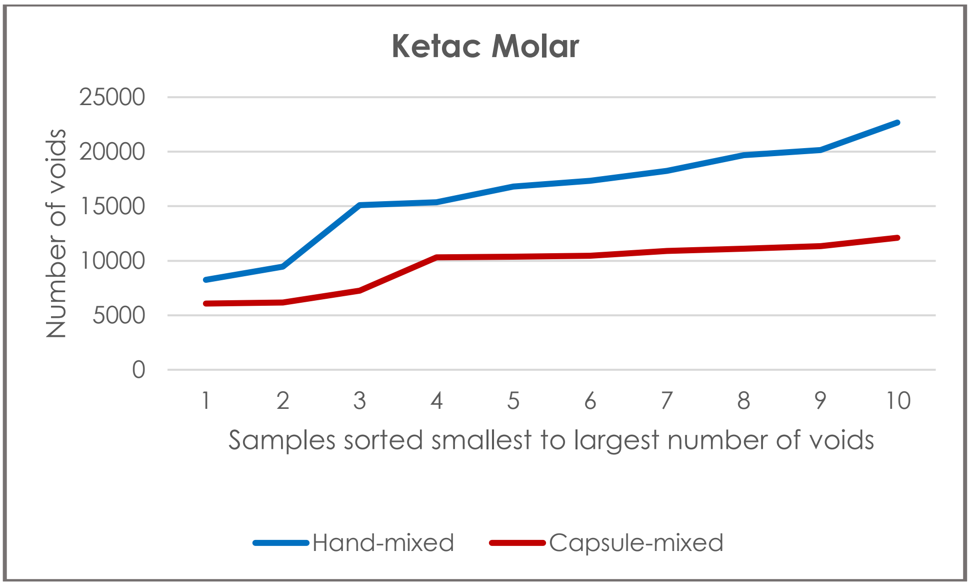

Figure 4.20: Mean values for the number of voids mean values in KMH and KMC specimens arranged in numerical order from smallest to largest values

Volume of voids

When the statistical data for the volume of voids for RSCH- and RSCC- paired groups were investigated, it was found that the means for the two groups differed by 0.482, which was statistically significant (p=0.005). The medians for the two groups differed by 0.737, which was also statistically significant (p=0.019). Table 4.13 provides a summary of the statistical analysis. Figure 4.21 graphically displays the mean values for the volume of voids in RSCH and RSCC with specimens arranged in numerical order from smallest to largest values.

Table 4.13: Statistical comparison of the volume of voids values of RSCH and RSCC

	RSCH	RSCC	p Value
n	10	10	
Mean (+- SD)	0.930 (0.283)	0.448 (0.388)	0.005*
Median (IQR)	0.967 (0.633-1.199)	0.230 (0.150-0.728)	0.019**
Min/Max	0.619/1.263	0.08/1.117	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

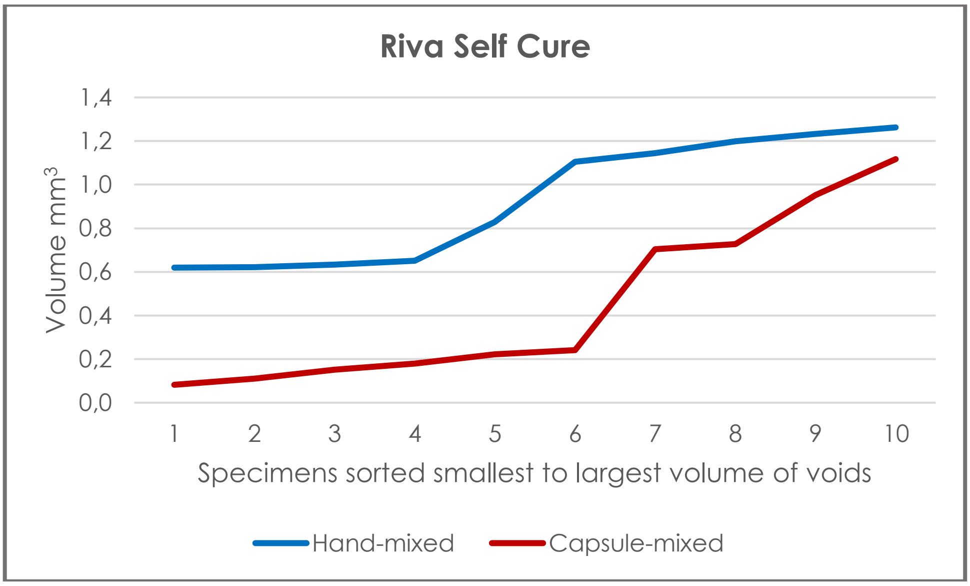

Figure 4.21: Mean values for the volume of voids in RSCH and RSCC specimens arranged in numerical order from smallest to largest values

The statistical data for the volume of voids for FIXH- and FIXC- paired groups were examined, and it was determined that the means for the two groups differed by 0.529, which was statistically significant (p<0.001). The medians for the two groups differed by 0.628, which was also statistically significant (p<0.001).

Table 4.14 provides a summary of the statistical analysis. Figure 4.22 graphically depicts the mean values for the volume of voids in FIXH and FIXC with specimens arranged in numerical order from smallest to largest values.

Table 4.14: Statistical comparison of the volume of voids values of FIXH and FIXC

	FIXH	FIXC	p Value
n	10	10	
Mean (+- SD)	0.339 (0.083)	0.868 (0.199)	<0.001*
Median (IQR)	0.316 (0.289-0.402)	0.9440 (0.692-0.988)	<0.001**
Min/Max	0.231/0.470	0.489/1.109	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

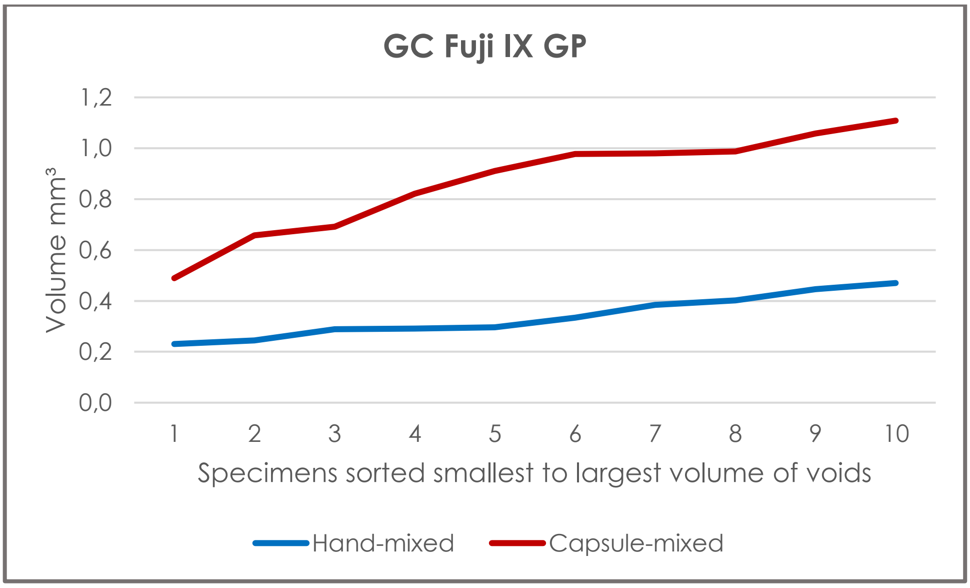

Figure 4.22: Mean values for the volume of voids mean values in FIXH and FIXC specimens arranged in numerical order from smallest to largest values

When comparing the statistical data for the volume of voids for KUH- and KUC-paired groups, the difference between the two groups' means was 0.287, which was statistically significant (p=0.004). The difference between the medians of the two groups was 0.275, which was also statistically significant (p=0.007).

Table 4.15 provides a summary of the statistical analysis. Figure 4.23 graphically represents the mean values for the volume of voids in KUH and KUC with specimens arranged in numerical order from smallest to largest values.

Table 4.15: Statistical comparison of the volume of voids values of KUH and KUC

	KUH	KUC	p Value
n	10	10	
Mean (+- SD)	0.519 (0.198)	0.232 (0.194)	0.004*
Median (IQR)	0.495 (0.41-0.58)	0.220 (0.040-0.398)	0.007**
Min/Max	0.260/0.870	0.030/0.570	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

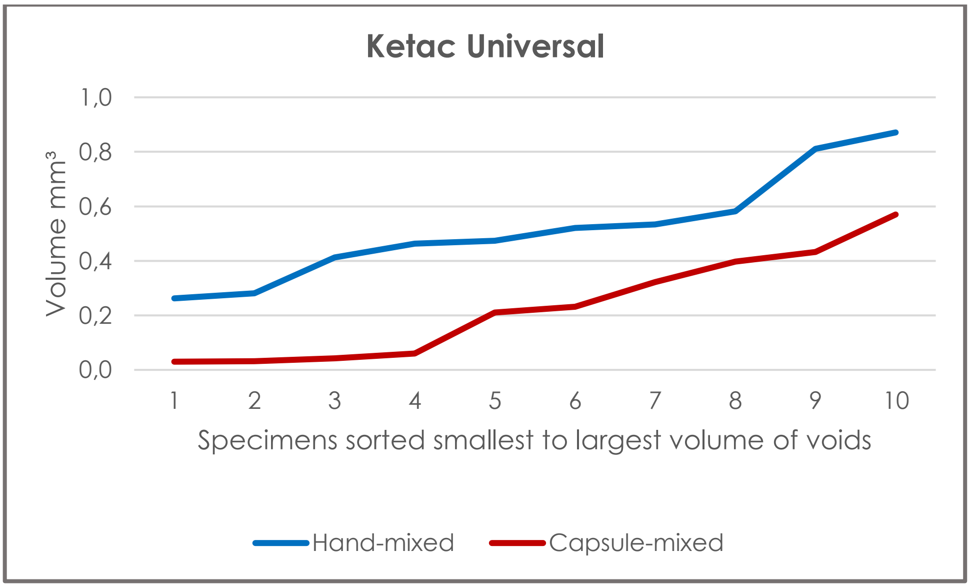

Figure 4.23: Mean values for volume of voids in KUH and KUC specimens arranged in numerical order from smallest to largest values

When the statistical data for the volume of voids for KMH- and KMC- paired groups was compared, the difference between the two groups' means was 0.18, which was statistically significant (p=0.010). The difference between the medians of the two groups was 0.149, which was also statistically significant (p=0.008).

Table 4.16 provides a summary of the statistical analysis. Figure 4.24 graphically displays the mean values for the volume of voids in KMH and KMC with specimens arranged in numerical order from smallest to largest values.

Table 4.16: Statistical comparison of the volume of voids values of KMH and KMC

	KMH	**KMC**	**p Value**
n	10	10	
Mean (+- SD)	0.525 (0.172)	0.345 (0.060)	0.010*
Median (IQR)	0.504 (0.456-0.699)	0.355 (0.326-0.386)	0.008**
Min/Max	0.203/0.757	0.232/0.413	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

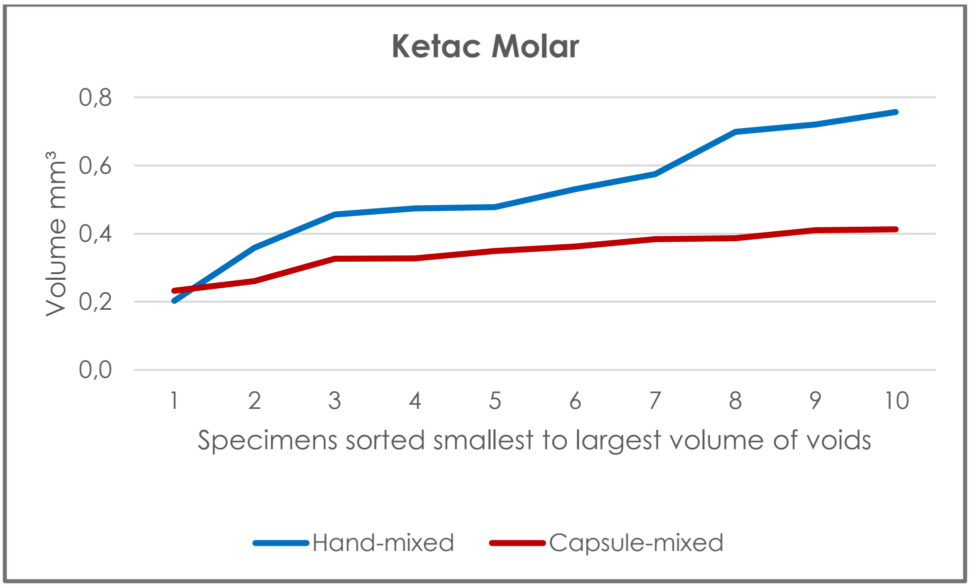

Figure 4.24: Mean values for the volume of voids in KMH and KMC specimens arranged in numerical order from smallest to largest values

Volume percentage of voids

The statistical data for the volume percentage of voids of RSCH- and RSCC-paired groups exhibited a difference of 0.802 in means values for the two groups, which was statistically significant (p=0.005). In addition, the medians for the two groups differed by 1.227, which was also statistically significant (p=0.019). Table 4.17 provides a summary of the statistical analysis. Figure 4.25 graphically displays the mean values for the volume percentage of voids in RSCH and RSCC with specimens arranged in numerical order from smallest to largest values.

Table 4.17: Statistical comparison of the volume percentage of voids of RSCH and RSCC

	RSCH	RSCC	p Value
n	10	10	
Mean (+- SD)	1.548 (0.471)	0.746 (0.645)	0.005*
Median (IQR)	1.610 (1.054-1.996)	0.383 (0.250-1.212)	0.019**
Min/Max	1.031/2.102	0.133/1.860	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

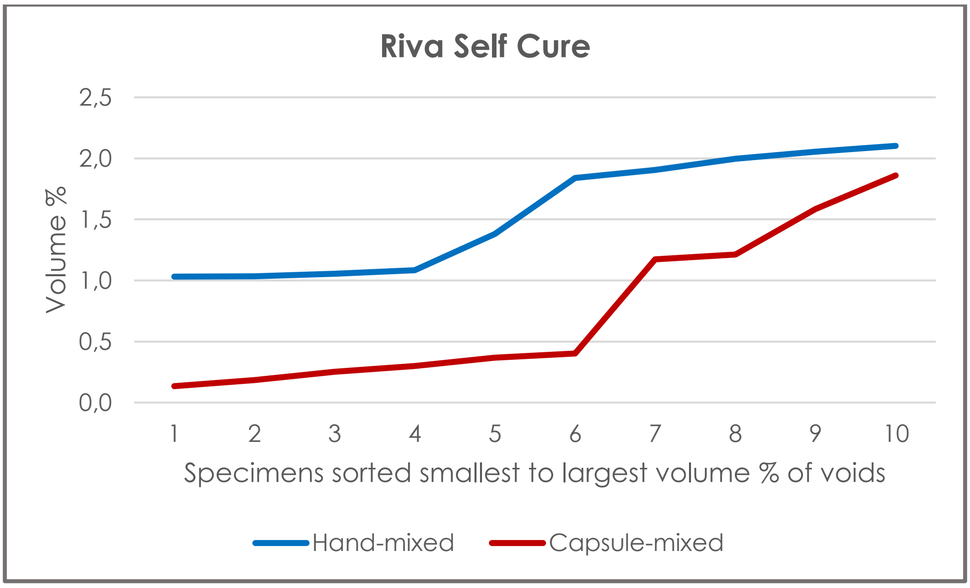

Figure 4.25: Mean values for the volume percentage of voids in RSCH and RSCC specimens arranged in numerical order from smallest to largest values

When the statistical data for the volume percentage of voids of FIXH- and FIXC-paired groups was compared, the means differed by 0.882 for the two groups, which was statistically significant (p<0.001). In addition, the medians for the two groups differed by 1.046, which was also statistically significant (p<0.001). Table 4.18 provides a summary of the statistical analysis. Figure 4.26 graphically depicts the mean values for the volume percentage of voids in FIXH and FIXC with specimens arranged in numerical order from smallest to largest values.

Table 4.18: Statistical comparison of the volume percentage of voids of FIXH and FIXC

	FIXH	FIXC	p Value
n	10	10	
Mean (+- SD)	0.564 (0.138)	1.446 (0.331)	<0.001*
Median (IQR)	0.526 (0.480-0.670)	1.572 (1.152-1.645)	<0.001**
Min/Max	0.384/0.783	0.815/1.846	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

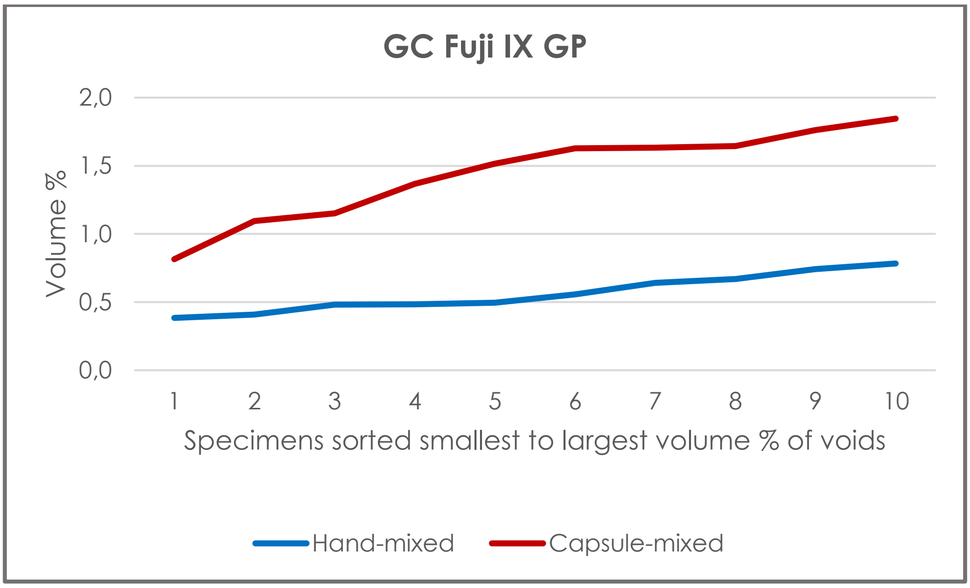

Figure 4.26: Mean values for the volume percentage of voids in FIXH and FIXC specimens arranged in numerical order from smallest to largest values

The statistical data for the volume percentage of voids of KUH- and KUC-paired groups presented with a difference of 0.478 when the means for the two groups were compared, which was statistically significant (p=0.004). The medians for the two groups differed by 0.458, which was also statistically significant (p=0.006).

Table 4.19 provides a summary of the statistical analysis. Figure 4.27 graphically represents the mean values of the volume percentage of voids in KUH and KUC with specimens arranged in numerical order from smallest to largest values.

Table 4.19: Statistical comparison of the volume percentage of voids values of KUH and KUC

	KUH	KUC	p Value
n	10	10	
Mean (+- SD)	0.864 (0.330)	0.386 (0.322)	0.004*
Median (IQR)	0.824 (0.683-0.966)	0.366 (0.067-0.662)	0.006**
Min/Max	0.433/1.449	0.050/0.949	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

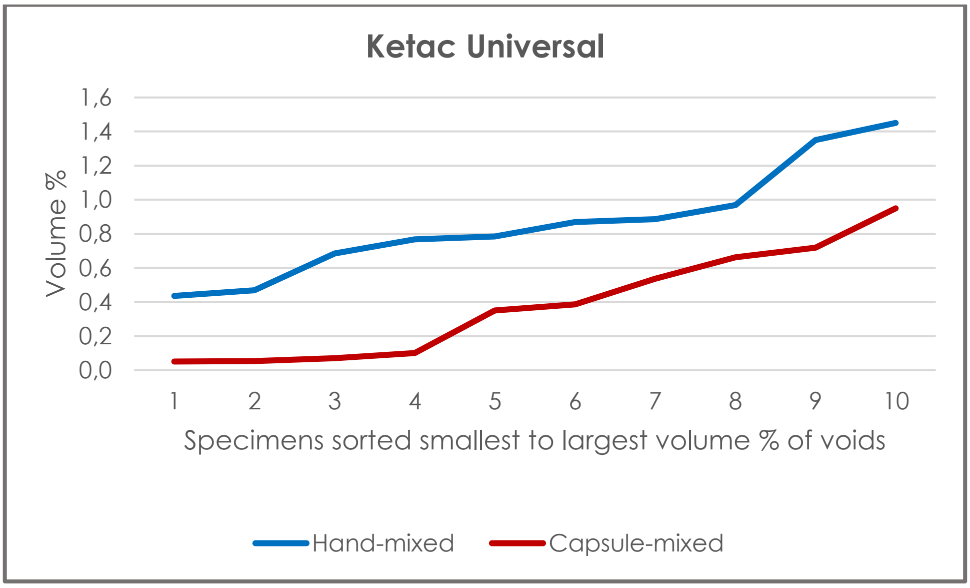

Figure 4.27: Mean values for the volume percentage of voids in KUH and KUC specimens arranged in numerical order from smallest to largest values

The statistical data for the volume percentage of voids of KMH- and KMC-paired groups were investigated. The means for the two groups varied by 0.299, which was statistically significant (p=0.010). The medians for the two groups varied by 0.247, which was also statistically significant (p=0.008).

Table 4.20 provides a summary of the statistical analysis. Figure 4.28 graphically displays the mean values for the volume percentage of voids in KMH and KMC with specimens arranged in numerical order from smallest to largest values.

Table 4.20: Statistical comparison of the volume percentage of voids values of KMH and KMC

	KMH	KMC	p Value
n	10	10	
Mean (+- SD)	0.874 (0.286)	0.575 (0.101)	0.010*
Median (IQR)	0.839 (0.759-1.163)	0.592 (0.543-0.643)	0.008**
Min/Max	0.337/1.260	0.387/0.687	

* Two sample t-test

** Non-parametric Wilcoxon rank sum test

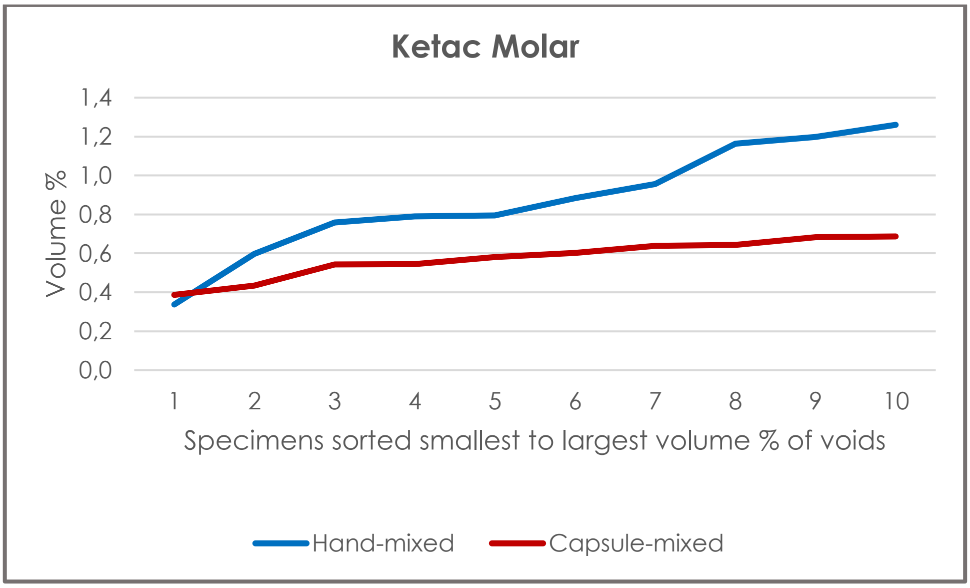

Figure 4.28: Mean values for the volume percentage of voids in KMH and KMC specimens arranged in numerical order from smallest to largest values

Micro-CT reconstructed 3D image analysis

A selection of Micro-CT reconstructed 3D images are included to give a visual indication of number of voids, sizes of voids, volume of voids and distribution of voids. Figure 4.29 represents the colour scale used to indicate the size of the voids in mm^3. The images for each product were selected according to the specimens with the smallest volume of voids and the specimens with the largest volume of voids. The cement matrix of the specimens is shown as opaque to highlight the presence of voids in colour.

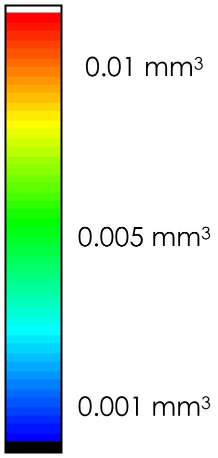

Figure 4.29: Colour scale for 3D reconstructed images of specimens indicating the size of the voids in mm^3

Figure 4.30 represents 3D reconstructed images of RSCH. Figure 4.31 represents 3D reconstructed images of RSCC.

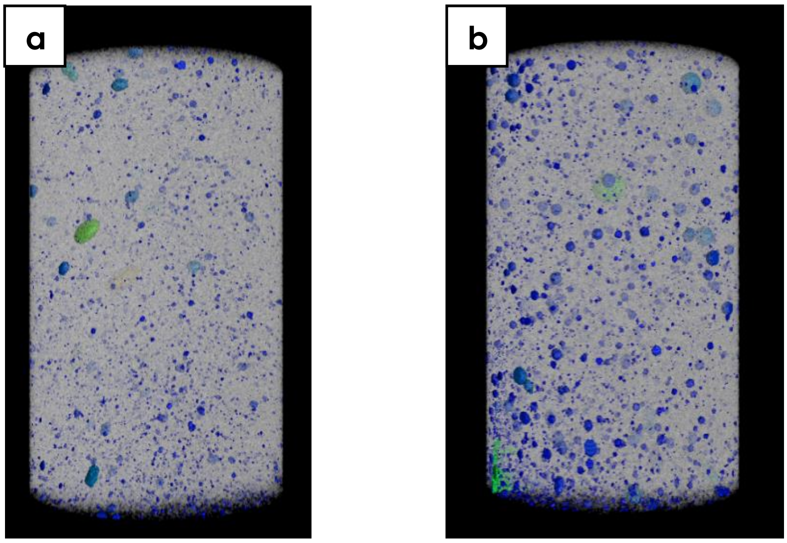

Figure 4.30: Micro-CT reconstructed images of RSCH with the a) smallest volume of voids and b) largest volume of voids

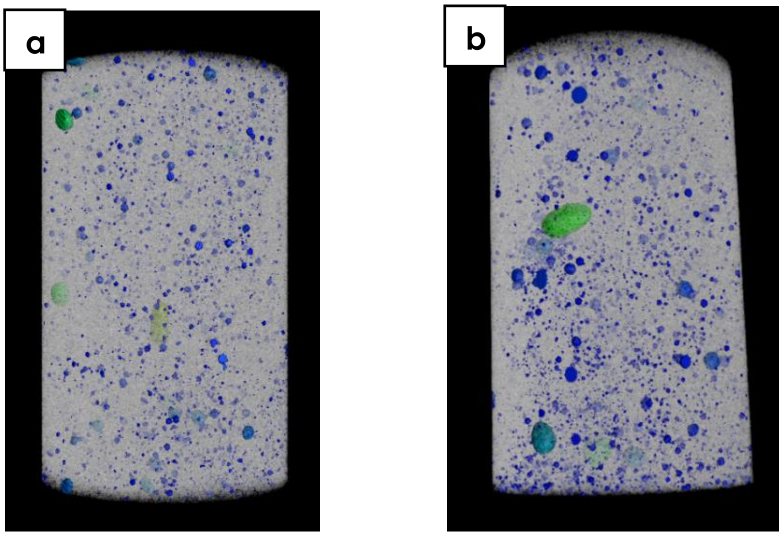

Figure 4.31: Micro-CT reconstructed images of RSCC with the a) smallest volume of voids and b) largest volume of voids

Figure 4.32 displays 3D reconstructed images of FIXH. Figure 4.33 displays 3D reconstructed images of FIXC.

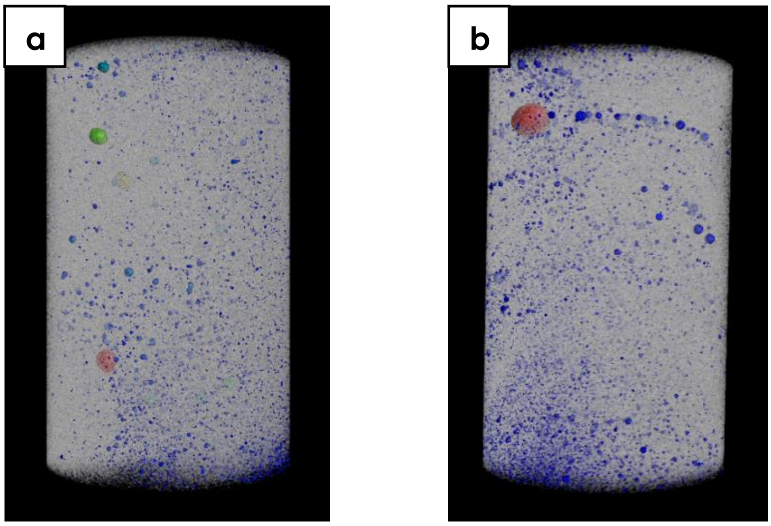

Figure 4.32: Micro-CT reconstructed images of FIXH with the a) smallest volume of voids and b) largest volume of voids

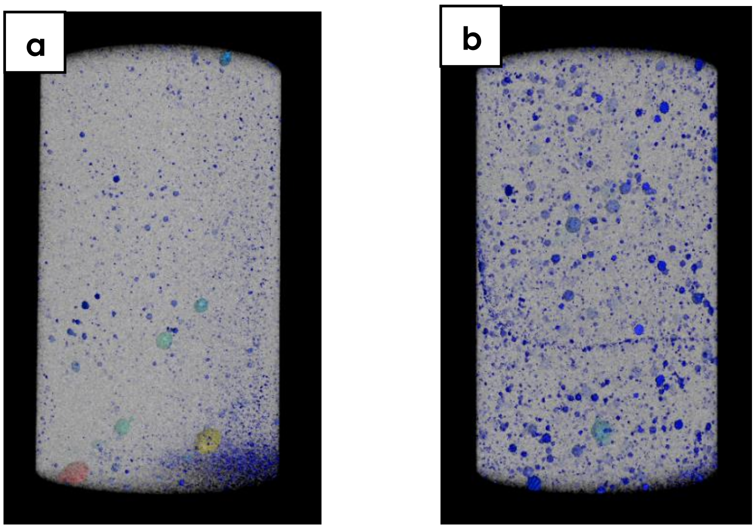

Figure 4.33: Micro-CT reconstructed images of FIXC with the a) smallest volume of voids and b) largest volume of voids

Figure 4.34 shows 3D reconstructed images of KUH. Figure 4.35 shows 3D reconstructed images of KUC.

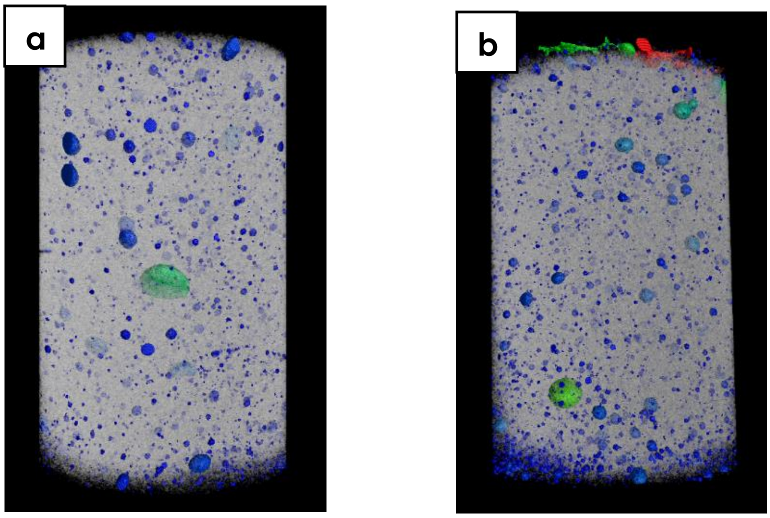

Figure 4.34: Micro-CT reconstructed images of KUH with the a) smallest volume of voids and b) largest volume of voids

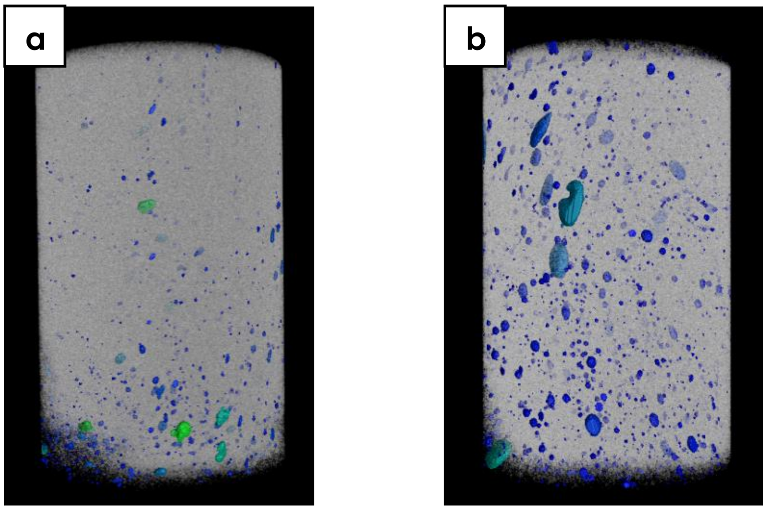

Figure 4.35: Micro-CT reconstructed images of KUC with the a) smallest volume of voids and b) largest volume of voids

Figure 4.36 exhibits 3D reconstructed images of KMH. Figure 4.37 exhibits 3D reconstructed images of KMC.

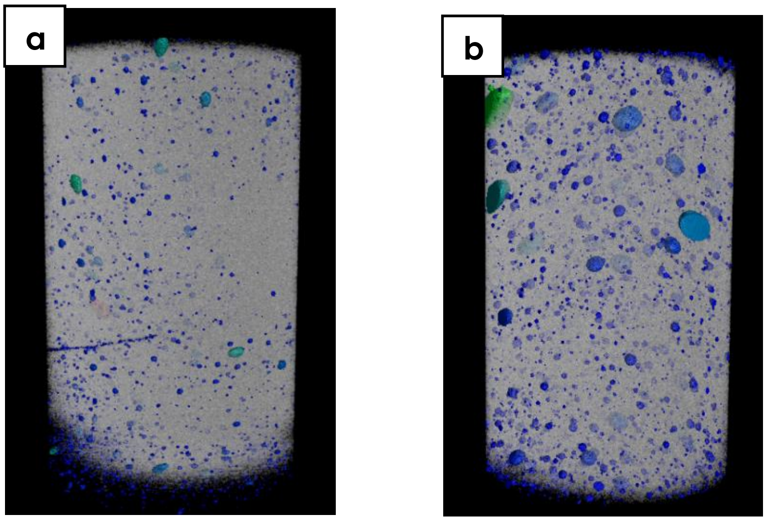

Figure 4.36: Micro-CT reconstructed images of KMH with the a) smallest volume of voids and b) largest volume of voids

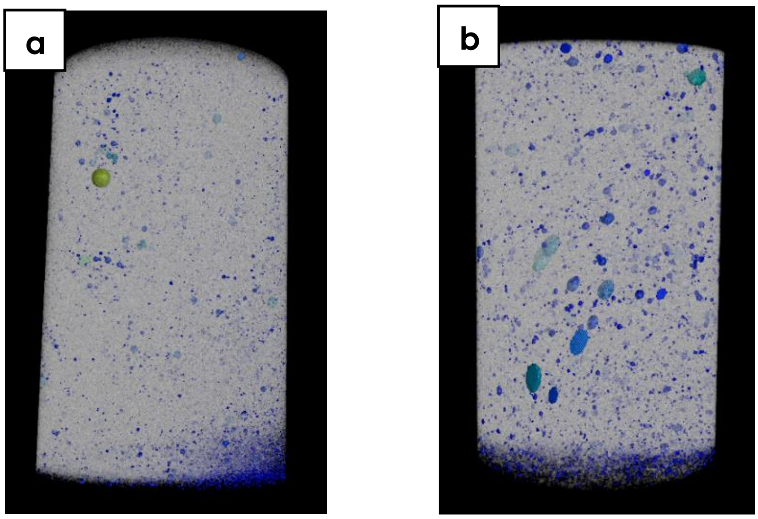

Figure 4.37: Micro-CT reconstructed images of KMC with the a) smallest volume of voids and b) largest volume of voids

Chapter 5: Discussion

Dental restorative materials and techniques are continuously advancing in an attempt to produce restorations with optimal mechanical properties, biological properties and aesthetics.[78,90] By testing the mechanical properties of a dental material, such as compressive strength, surface hardness and porosity, an indication to the durability and wear resistance of the tested material can be concluded.[90]

5.1 Compressive strength

The compressive strength of a material is defined as the ability within a material to resist forces that can fracture or crush a standard sample of the material.[108] Mastication forces are partially compressive.[78,109] Cohesion forces within a material provide resistance to compressive forces.[108] Compressive strength of a material can be used as a measure of the durability[78] and the brittleness of such a material.[108]

Statistically significant differences were found in the mean and median compressive strengths between the Riva Self Cure hand-mix and Riva Self Cure capsule-mix paired group specimens tested. The Riva Self Cure capsule-mix exhibited notable higher values for compressive strength when compared with the Riva Self Cure hand-mix values. The current study thus suggests that there is a clear advantage in the use of Riva Self Cure capsule-mix with respect to the difference in compressive strength values. Two separate studies, one done by Dionysopoulos *et al.*[111] and the second carried out by Mulder and

Mohamed[109] reported similar compressive strength values for Riva Self Cure capsule-mix, as reported in this present study.

No statistically significant differences were found between the mean and median compressive strengths of the GC Fuji IX GP hand-mix and GC Fuji IX GP capsule-mix specimens tested. The compressive strength values between the hand-mixed and capsule-mixed versions of GC Fuji IX GP were similar. One study by Fleming and Zala[7] found that GC Fuji IX GP hand-mix groups had much lower compressive strength values compared to GC Fuji IX GP capsule-mix groups. Contradictory results were reported by Dowling and Fleming.[42] They found significant higher compressive strength values for GC Fuji IX GP hand-mix groups mixed according to manufacturer's recommendations, in comparison with the GC Fuji IX GP capsule-mix groups, suggesting that hand-mixing of GC Fuji IX GP was more beneficial in terms of compressive strength.[42] The compressive strength values obtained in this current study were lower when compared to the manufacturer's in-house research results.[114]

The mean and median values for the compressive strength of Ketac Universal hand-mix and Ketac Universal Aplicap capsule-mix also exhibited no statistically significant differences, with both groups performing equally regarding compressive strength. Similar compressive strength values for these materials were obtained in research conducted by Dionysopoulos *et al*.[115] on Ketac Universal Aplicap capsule-mix. Compressive strength values for Ketac Universal hand-mix and Ketac Universal Aplicap capsule-mix obtained by in-house research of the manufacturer were higher than values obtained in the current study.[9,92] The research by Mulder and Mohamed[109] produced slightly lower compressive strength values for Ketac Universal Aplicap capsule-mix, when compared to the current study.

Definite statistically significant differences where encountered in the current study when the mean and median compressive strength values of Ketac Molar Easymix hand-mix and Ketac Molar Aplicap capsule-mix were compared. The Ketac Molar Aplicap capsule-mix displayed pronounced higher compressive strength values than Ketac Molar Easymix hand-mix. This suggests that Ketac Molar Aplicap capsule-mix should be advantageous for clinical use in situations where compressive strength is relevant. This finding is in agreement with the findings of Nomoto and McCabe[51], that also illustrated that Ketac Molar Aplicap capsule-mix performed better in relation to compressive strength compared to Ketac Molar Easymix hand-mix. Dowling and Fleming[42] conducted similar research and found no significant statistical differences between the mean compressive strengths of the Ketac Molar Easymix hand-mix and Ketac Molar Aplicap capsule-mix groups tested. The compressive strength values for Ketac Molar Aplicap capsule-mix in the current study correlate well with values obtained in research by Fleming *et al*.[98] on encapsulated glass ionomers.

Determining the correlation between mixing methods and mechanical properties of glass ionomer cements are complicated.[42,51] The chemical composition and setting phase progression are the two most critical factors regulating the properties.[51] In addition, the powder to liquid ratio also has an influence on the properties as it directly influences the concentration of reinforced glass fillers particles in the set cement.[51] The more powder added to a constant volume of liquid, the higher the concentration of reinforced glass fillers and the more resistant the product will be to compressive forces.[51] Reducing the powder content in relation to a constant volume of liquid, will reduce the reinforced glass filler content of the set cement and reduce the ability of the material to resist crack proliferation under compressive forces, negatively effecting the compressive strength of the product.[38] It has been reported by Billington *et al*.[43] that in clinical practice, glass ionomers with powder contents as low as 37% of the ratio recommended by the manufacturer, were used on a daily basis for hand-mixed glass ionomers. The findings of the research of Dowling and Fleming[38] concurred with these findings and postulated that powder contents below 50% of what manufacturers' recommend when hand-mixing, was commonplace in clinical practice.

Table 3.2 illustrates the powder/liquid ratios of the tested hand-mix and capsule-mix glass ionomers cements. For Riva Self Cure and GC Fuji IX GP the hand-mix powder/liquid ratios are slightly higher than that of the equivalent capsule-mix products. Ketac Universal Aplicap capsule-mix has a slightly higher powder/liquid ratio compared to Ketac Universal hand-mix. When the powder/liquid ratio of Ketac Molar Easymix and Ketac Molar Aplicap are compared, the powder/liquid ratio of Ketac Molar Easymix is substantially higher than that of Ketac Molar Aplicap. The powder of Ketac Molar Easymix is highly granulated, making the powder less dense, more flowable and more absorbent, which could explain the high powder/liquid ratio for this hand-mixed product.[116] The small or relatively larger differences in powder/liquid ratios between the hand-mix and equivalent capsule-mix products could possibly influence research results comparing mixing methods of glass ionomer cements. The challenge for manufacturers is to find the balance between the powder/liquid ratio, the polyacid concentration and the molecular weight of the polyacid to produce glass ionomers with optimal properties in either hand-mix and capsule-mix preparations.[2]

Voids in set cement occur either by insufficient wetting of the powder by the liquid, or by the inadvertent inclusion of air during the mixing procedure. Voids and the concentration of reinforced glass filler have a notable impact on the mechanical properties.[51] In the current study the SEM evaluations were only performed to illustrate the interrelation between compressive strength and voids present in a material. SEM images allow for the evaluation of the surface structure of a material, the presence of voids and the filler particle size and distribution.[41,78]

A descriptive analysis of the SEM images of the current study display voids or porosity of different sizes in all the specimen fragments examined. The microstructure and fracture mode of all tested specimen fragments were somewhat alike.[78] Fracture lines were observed both originating from the voids and running between the voids, which suggests that voids act as a sources of stress concentration.[7,52,54] The larger the voids and the more voids present, the greater the probability of fracture at lower levels of stress applied.[51] Research by Xie *et al*.[54] suggested that higher compressive strength values are related to more dense surface textures, less and smaller voids and smaller tightly packed glass filler particles. It can be postulated that surface irregularities because of porosity and cracks in conjunction with interior porosity and cracks contribute to material failure.[7]

5.2 Surface hardness

The definition of surface hardness is the ability of a material to resist permanent indentation or piercing when a force is applied to the material.[108] The harder the surface, the larger the hardness number (VHN) will be for Vickers hardness measurement.[108] Xie *et al*.[54] concluded that glass ionomers that contain glass particles of different shapes and sizes, with a highly fused glass particle-polymer matrix and dense surface texture will exhibit high surface hardness values.

The lack of statistically significant differences in VHN of Riva Self Cure hand-mix and Riva Self Cure capsule-mix suggests that for Riva Self-cure the hand-mix and capsule-mix resulting products exhibit approximately the same surface hardness. This suggests that there is no real advantage in terms of surface hardness to using either of the methods for mixing. Values reported by

Dionysopoulos *et al*.[111] and Mulder and Mohamed[109] for surface hardness of Riva Self Cure capsule-mix correlate with the values obtained in the current study for this measured property.

Significant statistical differences in the surface hardness were identified between the GC Fuji IX GP paired groups, Ketac Universal paired groups and between Ketac Molar paired groups. The capsule-mixed specimens of GC Fuji IX GP, Ketac Universal Aplicap and Ketac Molar Aplicap exhibited substantially increased hardness numbers (VHN) when compared to the hardness numbers (VHN) of the equivalent hand-mixed specimens for each respective material. When comparing surface hardness, the capsule-mixed versions of GC Fuji IX GP, Ketac Universal Aplicap and Ketac Molar Aplicap were superior to their hand-mixed equivalents in the current study. The Ketac Universal Aplicap capsule-mix surface hardness values correlate well with the hardness values reported by Alrahlah[110], as well as those published as in-house research by 3M ESPE.[9] The surface hardness values for Ketac Universal Aplicap capsule-mix in the current study were higher than values obtained by Dionysopoulos et al.,[111] and Mulder and Mohamed[109] The surface hardness values of GC Fuji IX GP capsule-mix are similar to those values published by GC as part of the company's in-house research on this product.[114]

The correct powder/liquid ratio of glass ionomer cements are crucial to durability, strength, working and setting time of the material.[41,109] Various studies have been done on a range of lower than recommended powder/liquid ratios of glass ionomer cements and the effects on the mechanical properties of the set cement.[7,109] Mulder and Mohamed[109] examined the powder/liquid ratios of capsulated glass ionomers from different manufacturers by deconstructing the capsules and the weighing the powder and liquid contents thereof. It was found that the powder/liquid ratios of most of the material batches tested were within the +10 % to -10 % range.[109] Capsules were also observed from the same manufacturers that had powder/liquid ratios above the +10 % of the manufacturer's recommendation which showed higher viscosity than normal which influenced the handling of the material.[109]

Manufacturers place precise values in grams for powder and liquid weights in product brochures and on product packaging/labels. Their in-house research is also based on these precise values.[109] The higher the volume of powder and/or the lower the volume of liquid, the shorter the working and setting time and the higher the compressive strength will be.[109] Final restorations mixed with a decreased powder/liquid ratio will be more susceptible to acid erosion.[109] Mulder and Mohamed[109] concluded that, provided the powder/liquid ratio of capsulated glass ionomers fall within +10 % to -10 % of the manufacturer's recommendations, the compressive strength and surface hardness of the set product will not be adversely affected.

5.3 Porosity

In this study Micro-CT scanning was used to calculate porosity in set glass ionomer cements. The Micro-CT system and software makes it possible to achieve non-invasive charting of microstructure in 3D by producing high resolution images and rapid data acquisition.[50,112]

Small air inclusions, dispersed throughout the entire mass of the cement, were observed in all the scanned glass ionomers cements specimens that were examined in this study. Larger air inclusions were also observed and these could contribute to material failure at lower stress forces, and might have a negative effect on the performance of the material.[50]

Hand-mixing of higher viscosity glass ionomer cement should produce an even diffusion of unreacted glass fillers throughout the plastic mass. If inadequate

spatulation force is used, clumps of unreacted glass filler powder will form rather than even diffusion of powder particles.
Voids or porosity have been identified in these powder clumps in a previous study by Fleming and Zala.[7] It has also been shown that cracks or fractures will most likely commence from these sites.[7]

According to another study by Fleming *et al*.[41] porosity may be introduced during hand-mixing when a greater volume of powder is added to the liquid volume than that which is recommended by the manufacturer. A greater volume of powder will require an increased pressure during spatulation to sufficiently mix the material mass, which could lead to greater porosity in the end product.[41] Using a lower than recommended powder volume to liquid volume resulted in reduced porosity, but this simultaneously affected the strength of the cements negatively due to the lower concentration of reinforced glass filler particles in the set cement.[41] Studies have also pointed out that increased porosity and larger voids in hand-mixed glass ionomer test specimens could be attributed to air being incorporated in the specimen during filling of the moulds for specimen fabrication, which was more difficult than placing the capsule-mixed cement.[7,41]

No significant statistical differences were found between the mean values for number of voids of Riva Self Cure hand-mix and Riva Self Cure capsule-mix specimens tested. However, the mean values for the volume of voids and the volume percentage of voids in Riva Self Cure hand-mix and Riva Self Cure capsule-mix specimens differed significantly. The Riva Self Cure hand-mix exhibited notable higher mean values for volume of voids and volume percentage of voids when compared with Riva Self Cure capsule-mix mean values. This finding suggests that encapsulated Riva Self Cure is more beneficial for clinical use because of the lower volume of voids in the tested specimens and should out- perform Riva Self Cure hand-mix when mastication forces are applied to the product.

Interestingly, Riva Self Cure capsule-mix specimens also showed improved performance when compressive strength was tested, which can be linked to the reduced volume of voids calculated in the Riva Self Cure capsule-mix specimens.

GC Fuji IX GP capsule-mix showed noticeable higher values for volume of voids and volume percentage of voids compared to GC Fuji IX GP hand-mix. The results could possibly be explained by operator induced variability, although utmost care was taken to accurately measure the powder and liquid volumes according to manufacturer's recommendations. Dowling and Fleming[38] speculated that powder contents as low as 50 % of manufacturer's recommendations would not be unusual in clinical practice. If the measured powder volume was lower than recommended by the manufacturer in relation to the liquid measured, the volume of porosity would be less for the hand-mixed product according to Fleming *et al*.[41] If the measured liquid volume was possibly more than the manufacturers' recommendations in relation to the measured powder volume, the effect would be the same.[41] Spatulation time of hand-mixed products are automatically longer than capsule-mixed products and this could also have resulted in a more homogeneously hand-mixed product with less voids, compared to the capsule-mixed resulting product.[42,52]

Al-Kadhim *et al*.[117] compared data for hand-mixed and capsulated glass ionomer luting cement and showed that the capsule-mixed product had larger voids and an increased volume of voids than the hand-mixed equivalents. The low viscosity of glass ionomer luting cements, compared to restorative glass ionomer cements with a higher viscosity, could be responsible for this result as concluded in the research of Nomoto and McCabe[51] where conventional mechanical mixing introduced a type of foam or frizz in low-viscosity cement. Kausnik *et al*.[52] compared voids present in restorative glass ionomer cements and came to the conclusion that capsule-mixed products contained more voids per volume than hand-mixed product. Conventional mixing machines, without centrifugation, as used with GC Fuji IX GP capsule-mix, may introduce increased porosity in some capsulated glass ionomer cements.[7]

The compressive strength values for GC Fuji IX GP capsule-mix did not significantly differ from GC Fuji IX GP hand-mix, which contradicts the possible relation between compressive strength and volume of porosity in Glass Ionomer products, as GC Fuji IX GP capsule-mix contained significantly higher volume of voids in the specimens tested and should have exhibited significant lower compressive strength values than GC Fuji IX GP hand-mix. The strontium-based powder of GC Fuji IX GP products might explain these results as strontium has an increased strengthening effect in GC Fuji IX GP products[118], the volume of voids appear to have little effect on the compressive strength of the set cement with regards to GC Fuji IX GP capsule-mix. Strontium is also responsible for the "snapset" characteristics of GP Fuji IX GP according to the manufacturer.[118]

Ketac Universal Aplicap capsule-mix and Ketac Molar Aplicap capsule-mix were mixed according to manufacturer's instructions in the Rotomix mechanical mixer. The reduced volume of voids and volume percentage of voids in Ketac Universal Aplicap capsule-mix and Ketac Molar Aplicap capsule-mix can possibly be attributed to the added centrifugal action of the Rotomix when mechanically mixing these products. Centrifuging should move air bubbles to the surface, allowing the air to "break out" before the mixing is completed.[7] Research has shown the added centrifugal action only to be beneficial for some cements and that the performance is dependent on the initial viscosity of the cement mass.[7,51] Glass ionomer cements mixed in the Rotomix also showed decreased working and setting times due to prolonged mixing caused by centrifuging after rotation according to research by Fleming *et al*.[7]

Issa *et al*.[119] examined the extrusion force, surface pH (indicating homogeneity), and porosity of capsulated glass ionomer cement when mixed with the Rotomix, by hand and or with a conventional Amalgamator and found the Rotomix more beneficial when the examined properties were compared.

Another probable solution to porosity in glass ionomer cements has been suggested by Coldebella *et al*.[105] The researchers applied ultrasonic excitation during the early setting reaction of glass ionomer specimens. The ultrasonic excitation resulted in a decrease in the size and number of voids in the tested specimens when compared to the control group specimens where ultrasonic excitation was not used.[105] The high-vibration frequency deformed the voids and caused the voids to collapse.[105] Research has also shown that ultrasonic wave application could improve the setting reaction between the glass particles and the polyacid, and will also break up powder particle clusters formed.[105] Higher compressive strength and surface hardness, and increased bonding to enamel has also been documented when ultrasonic vibration has been applied to glass ionomer cement during the early setting reaction.[105]

5.4 Limitations of the study

It is acknowledged that the present study had the following possible limitations:

- Internal porosity of hand-mixed glass ionomers may have been increased when filling the moulds with the mixed products, but utmost care was taken to avoid air inclusion.[7]

- It must also be noted that possible dehydration of specimen fragments might have occurred during the preparations for SEM evaluation, which could have contributed to crack proliferation.[78]

- A limitation of the Micro-CT system and the software used are that two voids are counted as a single large void if those two voids are in contact with each other.[50]

Chapter 6: Conclusions and recommendations

The results of the current study demonstrate that the mixing method can have a profound effect on the properties of dental glass ionomer cements, but the relationship is quite complicated. Materials within the same generic group from the same manufacturer show variations in the relationship between the method of mixing and the resulting mechanical properties.

With reference to Riva Self Cure, capsule-mixing was shown to be superior to the hand-mixing when compressive strength, volume of voids and volume percentage of voids results were compared. The values for surface hardness and number of voids did not significantly differ for Riva Self Cure capsule-mix and Riva Self Cure capsule-mix. This current study suggests that capsule-mixing of Riva Self Cure is probably more advantageous for clinical use.

When comparing GC Fuji IX GP capsule-mixing and hand-mixing, there were no significant differences in the compressive strength or the number of voids of the final set products. There were, however, significant differences in the surface hardness, volume of voids and volume percentage of voids. GC Fuji IX GP capsule-mix performed better in surface hardness tests. GC Fuji IX GP hand-mix showed a notably lower volume of voids and volume percentage of voids when compared to GC Fuji IX GP capsule-mix. The results for GC Fuji IX GP are inconclusive on whether the capsule-mix or the hand-mixed product are superior based upon the properties examined for the purposes of the current research study.

Ketac Universal capsule-mix out-performed Ketac Universal hand-mix in surface hardness, number of voids, volume of voids and volume percentage of voids. The values for the compressive strength of Ketac Universal capsule-mix were higher than those of Ketac Universal hand-mix, but this difference was not statistically significant. Ketac Universal Aplicap capsule-mix is recommended for clinical use in the current study.

Ketac Molar Easymix hand-mix under-performed when compared with Ketac Molar Aplicap capsule-mix with regards to compressive strength, surface hardness, number of voids, volume of voids and volume percentage of voids. In this current study there is a clear advantage in the use of Ketac Molar Aplicap capsule-mix and consequently Ketac Molar Aplicap capsule-mix is advocated for use in clinical practice.

Dentists in clinical practice might consider the Rotomix from 3M ESPE for mechanical mixing of capsulated glass ionomer cements. The 3M products mixed with this machine in the current study showed a pronounced reduction in the number of voids, the volume of voids and the volume percentage of voids when compared to the other products tested in the current study. The added centrifugal action together with rotational action of the Rotomix most likely explains this reduction. Most research suggests that a reduction in the volume of voids will result in increased compressive strength of the set cement and one can even postulate that an increase in surface hardness can also be expected. A follow-up study specifically aimed at using the Rotomix for the mixing of all the tested capsulated glass ionomer materials will provide valuable information and more conclusive results.

For glass ionomer cements to function at their optimum, the correct powder/liquid ratio, viscosity, mixing method and mixing time is of utmost importance. Altering any of these parameters will negatively affect the performance of the set product.

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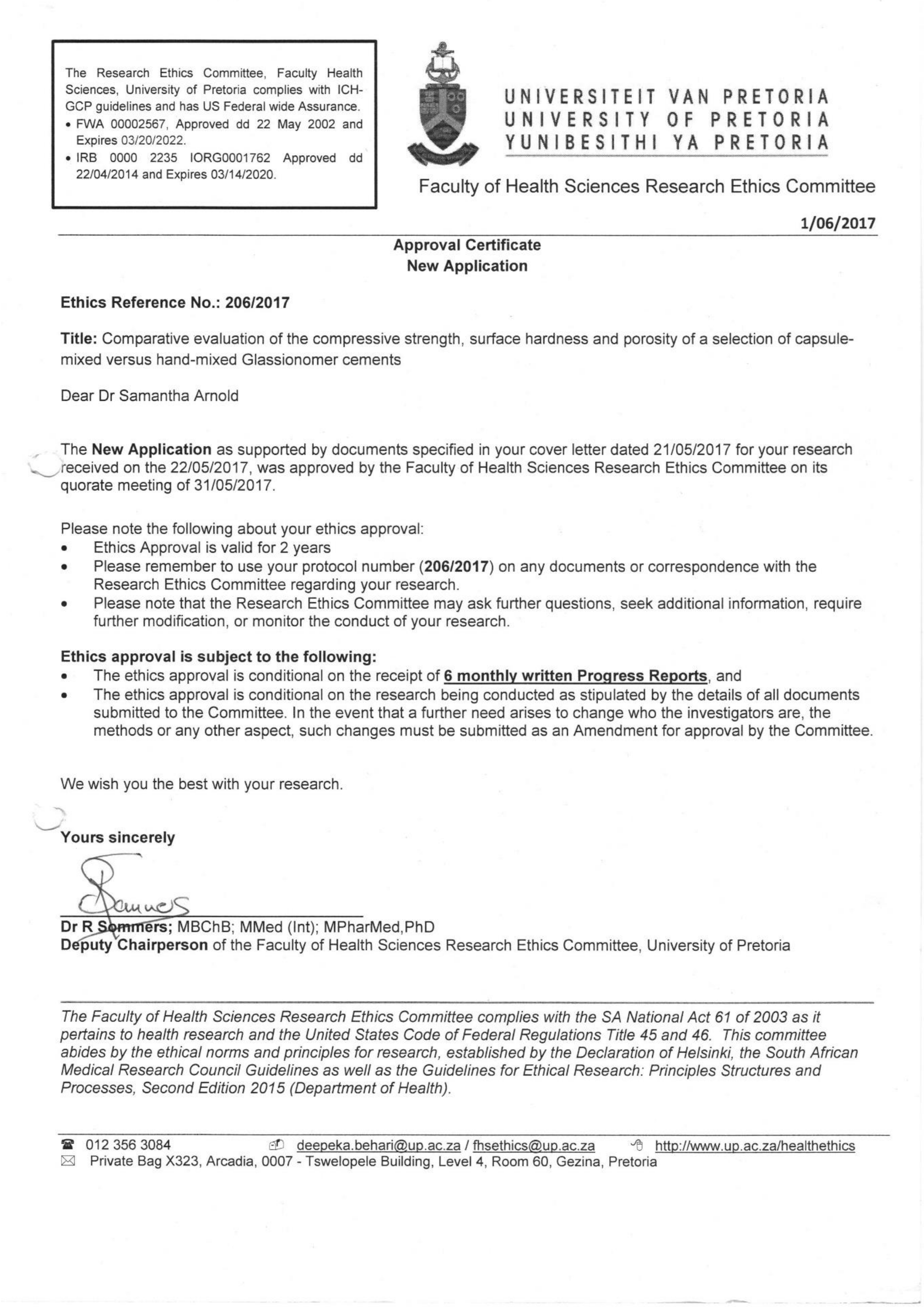
Appendix A: Ethical clearance



The Research Ethics Committee, Faculty Health Sciences, University of Pretoria complies with ICH-GCP guidelines and has US Federal wide Assurance.

- FWA 00002567, Approved dd 22 May 2002 and Expires 03/20/2022.
- IRB 0000 2235 IORG0001762 Approved dd 22/04/2014 and Expires 03/14/2020.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Faculty of Health Sciences Research Ethics Committee

1/06/2017

Approval Certificate
New Application

Ethics Reference No.: 206/2017

Title: Comparative evaluation of the compressive strength, surface hardness and porosity of a selection of capsule-mixed versus hand-mixed Glassionomer cements

Dear Dr Samantha Arnold

The **New Application** as supported by documents specified in your cover letter dated 21/05/2017 for your research received on the 22/05/2017, was approved by the Faculty of Health Sciences Research Ethics Committee on its quorate meeting of 31/05/2017.

Please note the following about your ethics approval:

- Ethics Approval is valid for 2 years
- Please remember to use your protocol number (**206/2017**) on any documents or correspondence with the Research Ethics Committee regarding your research.
- Please note that the Research Ethics Committee may ask further questions, seek additional information, require further modification, or monitor the conduct of your research.

Ethics approval is subject to the following:

- The ethics approval is conditional on the receipt of **6 monthly written Progress Reports**, and
- The ethics approval is conditional on the research being conducted as stipulated by the details of all documents submitted to the Committee. In the event that a further need arises to change who the investigators are, the methods or any other aspect, such changes must be submitted as an Amendment for approval by the Committee.

We wish you the best with your research.

Yours sincerely

Dr R Sommers; MBChB; MMed (Int); MPharMed,PhD
Deputy Chairperson of the Faculty of Health Sciences Research Ethics Committee, University of Pretoria

The Faculty of Health Sciences Research Ethics Committee complies with the SA National Act 61 of 2003 as it pertains to health research and the United States Code of Federal Regulations Title 45 and 46. This committee abides by the ethical norms and principles for research, established by the Declaration of Helsinki, the South African Medical Research Council Guidelines as well as the Guidelines for Ethical Research: Principles Structures and Processes, Second Edition 2015 (Department of Health).

☎ 012 356 3084 deepeka.behari@up.ac.za / fhsethics@up.ac.za http://www.up.ac.za/healthethics
✉ Private Bag X323, Arcadia, 0007 - Tswelopele Building, Level 4, Room 60, Gezina, Pretoria