Comparative *in vitro* study of selected physical properties of Activa, Cention N and Vitremer

A mini-thesis submitted in partial fulfillment of the requirements for the degree of MSc in Pediatric Dentistry,
The University of the Western-Cape.

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KEY WORDS

Acidic media

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Conventional glass ionomer cement (GIC)

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Physical properties

Resin-modified glass ionomer cement (RMGIC)

Surface roughness (Ra)

Vitremer

Weight loss

ABSTRACT

Background: This study aimed to determine the association between dimensional change and surface roughness (Ra) of Vitremer, Activa and Cention N after immersing them into two different media: acidic and artificial saliva media for the period of a year. Measurements were made at 10 time intervals during the observation period.

Methodology: This was a quantitative and qualitative study. For the quantitative part, a total of 60 specimens were tested, 20 specimens for each material. The 20 specimens were further divided into 10 specimens. Ten were immersed in acidic media and the rest in saliva media. A measurement of the weight, height, and Ra was carried out as follows: day 0, day 1, day 2, day 7, day 21, day 28, day 60, day 90, day 180 and day 365. Scanning electron microscopy (SEM) was used to examine the surface of each material qualitatively pre and post immersion in the two media.

For fluoride measurements, an additional five samples from each material were left suspended in the de-ionized water by the use of dental floss. The materials were moved to new specimen jars after the completion of day 1, 2, 3, 4, 5, 6, 7, 14, 21 and 28. All the specimen jars had been kept for the fluoride measurements.

Results: Non-parametric tests were used to analyze the data. Linear regression analysis was used to measure the association between weight, height or surface roughness (Ra) and immersion time for a year. The result of this test showed that Vitremer had a significant association between the weight (p = 0.000), height (p = 0.007) and Ra (p = 0.001) when it was immersed in acidic media. On the other hand, when Vitremer was immersed in saliva media, only the weight variable showed a significant association (p = 0.002). For Cention N, significant association was found for only Ra when immersed in acidic media (p = 0.000). Finally, for Activa, all the studied associations; the weight, height and Ra in both media were found to be insignificant.

For saliva media, there was a significant weight change between the three materials during all 10 periods of time (p = 0.000). In the first six months, Cention N demonstrated

a significant increase in weight changes followed by Vitremer, then Activa. Yet, after a year, the difference between Cention N and Vitremer became insignificant and Activa showed the least weight changes. There was not a significant difference between the materials in terms of height and Ra measurements. The fluoride experiment was not successful due to technical issues during pH measurements of the collected solutions.
For comparison of the studied parameters between the three materials, the Kruskal-Wallis test was used. In acidic media, there was a significant difference between the materials in term of weight change in 10 periods of time (p = 0.000). In particular, after a two month period, Cention N had the highest weight, followed by Vitremer and then by Activa. The difference between Vitremer and Activa became insignificant throughout the rest of the experimental time frame. All the height measurements between the three materials were found to be insignificant except for day 365 (p = 0.048), where both Activa and Cention N were found to be significantly higher than Vitremer. For the Ra comparison, in the first two weeks, particularly day 1, 7 and 14, Cention N had significantly the lowest Ra among the other materials. As the three materials aged in the acidic media (day 180), Vitremer had significantly the highest Ra values. Cention N showed higher Ra values than Activa; nonetheless this difference was not significant.

The SEM images showed loss of some particles in all post-experimental images of the materials in acidic media. Vitremer showed the widest cracks with the loss of fillers. In saliva media, there was also loss of particles but to a lesser extent than in acidic media. Yet, the post-experimental image of Activa in saliva resembled the pre-experimental one.

Conclusion: Within the limitations of the study, the best material to resist Ra from prolonged acidic attack was Activa followed by Cention N and then Vitremer. Except for Vitremer, no significant changes in the Ra of the other materials were detected when the three materials were immersed in saliva media in the long term.

In acidic media Vitremer tended to lose weight and height faster than Cention N and Activa over a year. Cention N is the best material to resist dimensional change. However, in artificial saliva Vitremer gained water rapidly. Activa did not absorb a lot of

water and did not reject a lot of water; Activa demonstrated good dimensional stability and this property may be beneficial when compared to the other two materials tested.

The clinical significance of the study: All the materials studied were subjected to dimensional and Ra changes following long-term exposure to acidic substances, but the newer materials (Cention N and Activa) seemed to be more dimensionally stable and resistant to Ra changes than the older, well-known material (Vitremer). This may influence a clinician's choice of restorative material for use in pediatric dentistry.

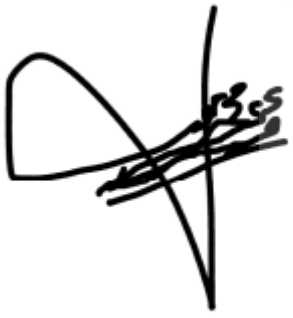
DECLARATION

I declare that "*Comparative in vitro study of selected physical properties of Activa, Cention N and Vitremer"* is my own work. It has not been submitted before for any degree or examination at any other university and that all the sources I have used or quoted have been indicated and acknowledged as complete references. I declare that I have no competitive interest in any of the companies that manufacture any of the materials used in this study. No shares and or stocks are held nor will I have any financial gain or loss with the publication of any manuscript and articles pertaining to this research.

Student number: 3819336

Date: 26th March 2021

Signed:



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Sincerely,

Ro'aa Mohammed Jafar

DEDICATION

This mini-thesis is dedicated to my beloved parents: Fathia Seed Ahmed and Mohammed Jafar.

To my beautiful Mom,

I still remember the day when you said to me: Ro'aa! Go for it and travel outside and I'm pretty sure that you will make me proud!

To the best dad ever,

I also still remember one of my last days at school; the chemistry final year exam. I was actually totally upset and down when you said to me,

You are capable of making a solution to everything! I totally trusted you! And when the result is out I find myself got the full mark!

To my sisters, Nuha, Duha and little Zulfa

To my brother, Tariq and my twin Mazin

To my students,

Thanks for giving me the feeling of continuous need for improvement. Rather, this mini-thesis would never been possible!

To the minority of dental practitioners; the left-handed operators,

It is not hard to specialize in a clinical field, just accept little of the back pain!

To the memory of the Sudanese angels who died in Khartoum massacre on the 3rd of June 2019.

Lastly, this work is dedicated to the bright ideas, to insatiable struggle, to infinite talent

To all of the readers!

Ro'aa

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LIST OF ABBREVIATIONS

µm	Micro-meter
ASPA	Alumino-Silicate Polyacrylic Acid
BMREC	Biomedical Research Ethics committee.
DENTREC	Dental Research committee
E	10^X or (Exponent)
g	Gram
GIC	Glass Ionomer Cement.
HEMA	Hydroxy-Ethyl-Methacrylate
LED	Light-Emitting Diode
MPa	Megapaschal
PMMA	Poly-methyl methacrylate
Ra	Surface roughness
RMGIC	Resin-modified glass ionomer cement
SEM	Scanning Electron Microscopy
UDMA	Urethane di-methacrylate

LIST OF ADDENDA

CHAPTER I: INTRODUCTION

Glass ionomers are used in clinical pediatric dentistry as full restorative materials (Correr *et al.*, 2012; Nicholson, 2018). The longevity of the restoration can be affected by both external and internal parameters. Consumption of acidic drinks among children could impact negatively the durability of glass ionomer cements (GICs) used to restore the primary teeth (Correr *et al.*, 2012). The current investigation focused on the impact of external and internal parameters on selected physical properties of materials found in the classification of GICs, through the use of a simulated acidic challenge and artificial saliva respectively.

1.1. Background

GICs were developed by Kent and Wilson around five decades ago in a form of polyalkenolate cement (Wilson & Kent, 1971; Nicholson, 1998; Webman *et al.*, 2016). The first generation of GIC underwent many processes in order to produce the first commercial cement (from Alumino-Silicate Polyacrylic Acid (ASPA) I to ASPA IV) (Nagaraja Upadhya & Kishore, 2005). Starting from the foundation, ASPA I was produced in 1972 from a slow reaction between the glass and polyacrylic acid (Nagaraja Upadhya & Kishore, 2005). However, ASPA I had high moisture sensitivity, a long setting time and was prone to hydrolysis and dehydration (Nagaraja Upadhya & Kishore, 2005). After five years, Wilson & Crisp (1977) produced ASPA II by adding d-tartaric acid and fluoride to ASPA I in order to enhance the working time of this cement (Nagaraja Upadhya & Kishore, 2005). However, the jelly-like structure of ASPA II pushed the authors to modify it by the addition of methyl-alcohol to produce ASPA III (Nagaraja Upadhya & Kishore, 2005). Although ASPA III had better physical properties than ASPA II, it was found to generate stains in the mouth (Nagaraja Upadhya & Kishore, 2005). Therefore, Wilson & Crisp (1977) synthesized “the first commercial cement’’ ASPA IV through interaction between acopolymer of acrylic and itaconic acid (Nagaraja Upadhya & Kishore, 2005; Webman *et al.*, 2016). **Figure (1.1)** shows the first generation of GIC.

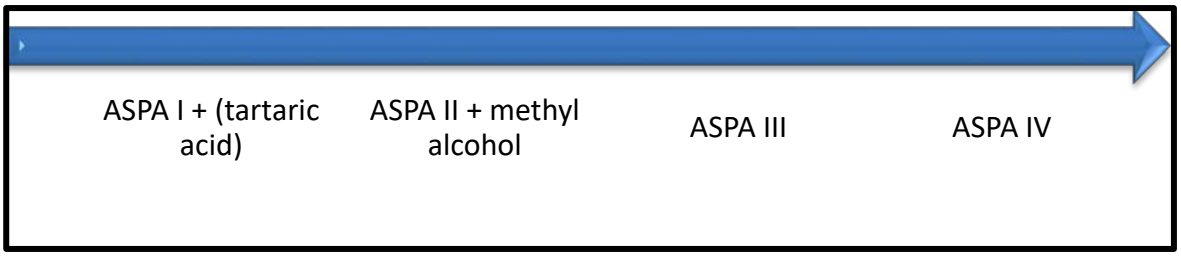


Figure (1.1): First generation glass ionomer cement.

However, first generation GIC still had poor physical properties (Iwami *et al*., 1998; Kim *et al.*, 1998; Nagaraja Upadhya & Kishore, 2005; Rodrigues *et al*., 2015; Samanta *et al.,* 2017). Hence, the second generation of GICs (or water hardened cements) emerged with further improvement in the manipulation (Nagaraja Upadhya & Kishore, 2005; Nicholson, 2016). This generation included the transference of poly-acrylic acid from a liquid to a powder state (Nagaraja Upadhya & Kishore, 2005). Hence, this generation was shown to provide a long shelf-life and strength to GICs (Nagaraja Upadhya & Kishore, 2005). Examples of the second generation of GICs are Chemfil, KetacCem, etc (Nagaraja Upadhya & Kishore, 2005).

1.2. Classification of Glass Ionomer Cements

Two classifications of GICs are mentioned in the literature. The GICs were sub-divided into different categories based on their compositions and indications for dental use (Castro & Feigal, 2002; Nagaraja Upadhya & Kishore, 2005). The first classification was based on the *composition of GICs*, which are conventional, hybrid, and polyacid modified composite resins (Castro & Feigal, 2002). However, the second classification was based on the *indications for use* (Nagaraja Upadhya & Kishore, 2005). For the latter classification, changes were made in the powder to liquid ratio and in the powder particle size, but not to the chemical compositions of the GIC (Nagaraja Upadhya & Kishore, 2005). Hence, GICs were divided into three types:

(1) Luting cement; used for crown, bridge and orthodontic brackets.

(2) Restorative cement; (which consists of aesthetic and reinforced subtypes) in order to be used in aesthetic areas and cervical caries.

(3) Lining or base cement (Prosser *et al.,* 1986; Nagaraja Upadhya & Kishore, 2005; Nicholson, 2018).

In this thesis, Vitremer considered to be a gold standard, well researched resin-modified GIC (RMGIC). It is a hand-mixed, powder/liquid material. Cention N is a powder/liquid hand mixed RMGIC termed an alkasite by the manufacturer, while Activa is a RMGIC mixed in a paste/paste system. Both Cention N and Activa are not well investigated.

1.3.Compositions

In general, the conventional GICs have two primary components: the liquid and the powder (Nicholson, 1998). The liquid consists of an estimated 45% polyacrylic acid, water and tartaric acid (Nicholson & Czarnecka, 2009). On the other hand, the powder is made of calcium fluoro-alumino-silicate glass particles (Sidhu, 2015; Nicholson, 2016). In particular, components of the powder are silica (SIO_2), Alumina (AL_2O_3) and calcium fluoride (CaF_2) (Nicholson & Czarnecka, 2009). Other components could also be present in the powder such as calcium oxide, aluminum phosphate and sodium aluminum fluoride (Nicholson & Czarnecka, 2009). However, RMGIC is composed of two additional components: the monomer, such as (10 - 15%) hydroxy-ethyl methacrylate (HEMA) in Vitremer for instance, and a camphorquinone (CQ) initiator (Mitra, 1991). In particular to Vitremer, the side chain was modified at the vinyl groups to form a cross-link between the polymer in the polymerization reaction as shown in **Figure (1.2)** (Nicholson, 1998).

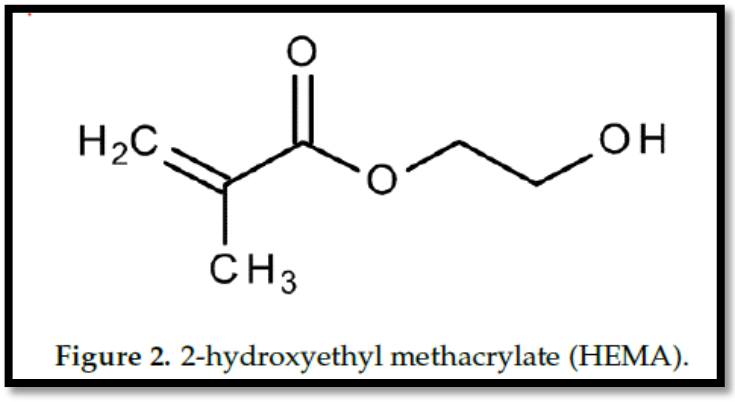


Figure 2. 2-hydroxyethyl methacrylate (HEMA).

Figure (1.2): Chemical structure of HEMA (Sidhu & Nicholson, 2016).

1.4. Setting reaction

GICs are known to have a distinct acid-base setting reaction in relation to other tooth colored restorative materials (Wood & Hill, 1991; Sidhu, 2015; Nicholson, 2018) as shown in **Figure (1. 3)** below. This reaction also incorporates an ion exchange reaction with the tooth structure (Sidhu, 2015). It is important to mention that the method of mixing this cement will affect the setting reaction products; such as hand mixing or encapsulation (Yelamanchili & Darvell, 2008). Therefore, it is recommended to adhere to the manufacturer's instructions in order to produce the best mechanical properties of the set material (Yelamanchili & Darvell, 2008).

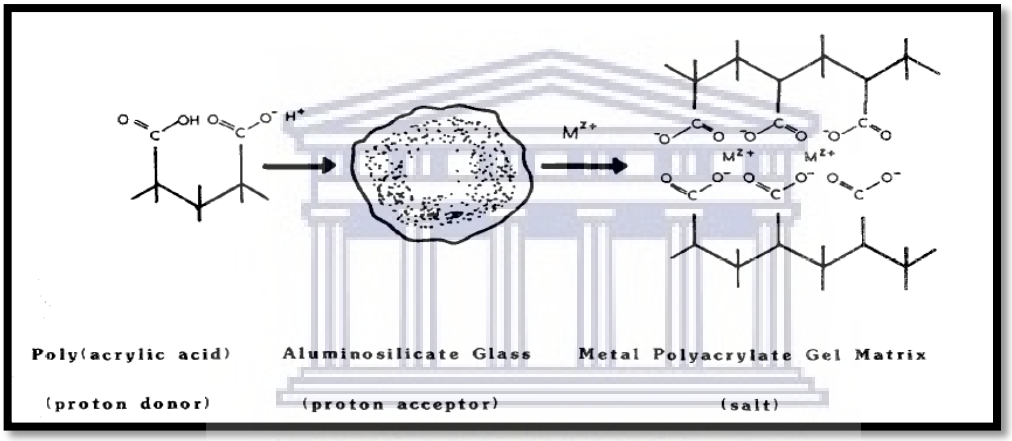


Figure (1.3): The setting reaction of the conventional GICs (Wood & Hill, 1991).

Following the continuous improvements in these materials and in order to reduce the drawbacks of the old cements, such as poor handling and the physical properties, an incorporation of resin was applied to the new material (Kim *et al*., 1998; Wilson, 1990; Mitsuhashi *et al.*, 2003; Sidhu, 2015; Webman *et al.*, 2016). This type of glass ionomer cement is called a resin-modified-glass ionomer cement (RMGIC) (Sidhu, 2015). These light-cured materials have a further additional polymerization reaction to the incorporated resin (Swift *et al.*, 1995; Kakaboura, *et al.*, 1996; Kim *et al.*, 2015; Sidhu, 2015). Therefore, this leads to improvement in wear, strength and fracture resistance (Wilson, 1990; Mitra, 1991; Mitsuhashi *et al.*, 2003; Sidhu, & Nicholson, 2016; Webman *et al.*, 2016; Finucane, 2019). A well-known example is Vitremer (3M ESPE, Paul, MN, USA) restorative material.

There is a debate in the literature whether the RMGICs are true GICs in terms of basic constituents and setting reactions (Mclean *et al*., 1994; Sidhu & Watson, 1995; Swift *et al.*, 1995; Kakaboura, *et al.*, 1996). Mclean *et al.* (1994) argued that in order for any material to be categorized as a RMGIC, the material should have ion leachable glass and a sufficient amount of water (Mclean *et al.*, 1994; Swift *et al.*, 1995). On the other hand, some authors categorized RMGICs as true GIC only if it has the ability to set in the dark (Sidhu & Watson, 1995; Kakaboura, *et al.*, 1996). More information about the setting mechanism of the materials included in the present study is provided and discussed in depth in the following chapter.

1.5. Advantages and disadvantages

The invention of RMGICs enhances the material working time with the advantage of the command set (Wilson, 1990). In addition, conventional and RMGICs have the ability to release and recharge fluoride (Hsu *et al.*, 2004; Moreau, *et al.*, 2010; Cabral *et al.*, 2015). Cavity sealing ability and reactivity to fluoride could play a role in the prevention of secondary caries and formation of an inhibition zone (Dunne *et al.*, 1996; Pereira *et al.*, 1998). Hence, conventional GICs and RMGICs were proven to be a good choice for restoration in the primary teeth (Qvist *et al.*, 2004; Cehreli *et al.*, 2013).

In addition, one of the main advantages of the GICs is an adequate cavity sealing ability (Van Meerbeek *et al.*, 2003; Van Dijken et *al.*, 2005; Mitra *et al.*, 2009). In general, adhesion of the GICs could be justified by two phenomena: 1) Mechanical interlocking due to self-adhesion in the submicron layer (Van Meerbeek *et al.*, 2003; Van Dijken et *al.*, 2005; Mitra *et al.*, 2009), 2) true chemical bonding through the formation of an ionic bond (Van Meerbeek *et al.*, 2003; Webman *et al.*, 2016). The chemical ‘‘ionic’’ bond is formed between the calcium of hydroxyapatite in tooth structure and the carboxylic group of the poly-alkenoic acid (Van Meerbeek *et al.*, 2003). This bond has been found for all types of the GICs (Yoshida *et al.*, 2000; Strassler, 2011; Alves *et al*., 2013). The process of the bonding starts by wetting of the surface, followed by formation of a hydrogen bond between the COOH group of the polymer and the water on the surface (Yoshida *et al.*, 2000; Van Meerbeek *et al.*, 2003). After the ionic exchange has taken place, an ionic bond is formed between the calcium ions in the hydroxyapatite and

COOH from the polymer (Yoshida *et al.*, 2000; Van Meerbeek *et al.*, 2003). In the long term, an ion interfacial zone started to develop (Van Meerbeek *et al.*, 2003).

Recently, in order to further improve the aesthetics and physical properties of the GICs, molecular nano-technology has been applied to RMGICs (Falsafi *et al.*, 2014; Sidhu, 2015; Khan *et al.*, 2019). Incorporation of nano-ionomers in the RMGICs has further advantages such as reduction of setting time and increase in compressive strength (Nicolson, 2016). As the particle size is reduced, the reactivity of the restoration will increase (Sidhu, 2015). Therefore, the setting of these small particles could be carried out prior to mixing (Sidhu, 2015). This technology was applied to some materials like Ketac Nano, Ketac N-100, and Equia system in order to restore teeth, especially in the smile line (Falsafi *et al.*, 2014; Sidhu, 2015; Khan *et al.*, 2019). Whether nano-ionomer is true glass ionomer cement or not is a topic of controversy in the literature (Flasfi *et al.*, 2014; Sidhu, 2015; Yao *et al.*, 2020) because some authors group these materials as composite materials. However, little work has been done regarding the application of the nano-technology in the GICs.

Figure (1.4): Sequence of change in the concept of improving GICs to RMGICs restorative materials over time.

With a significant rise in application of nano-technology in dentistry and tissue engineering, there is also a paradigm shift in dental research toward the bioactive restorative materials as shown in **Figure (1.4)** (Khan *et al.*, 2019). This research focus aims to combine the best biological, physical and mechanical properties of the restorative materials (Khan *et al.*, 2019). These materials have been called ‘’smart’’ due to their good interactions when facing a specific stimulus (Khan *et al.*, 2019). The stimulus could be stress, temperature, or change in pH (Khan *et al.*, 2019).

Activa and Cention N are restorative materials with claimed bioactivity (Activa Bioactive, 2016; Todd, 2016). Although evidence on these materials is lacking in the literature, particularly on their physical properties, some authors mentioned that these materials could have nano-particles which will improve their physical properties (Tiskaya *et al.*, 2019; Ruengrungsom *et al.*, 2020; Yao *et al.*, 2020).

1.6. Mechanical properties of new bioactive materials

For the wear resistance and the surface roughness, no comparative studies have been mentioned in the literature between Activa and other RMGICs materials. Hence, conclusive evidence about the mechanical properties of Activa bioactive is still limited and there is a major need for further *in vitro* and *in vivo* studies.

There are few studies in the literature on Cention N as well. However, most of the available literature is on microleakage (Castro & Feigal, 2002; Samanta *et al.*, 2017), and there are only two studies currently about the ion release of Cention N in relation to Activa (Tiskaya *et al.*, 2019; Ruengrungsom *et al.*, 2020). Furthermore, investigation of the long term wear or weight changes of Cention N in the long term, is lacking in the literature

In the current study, the aim was to report the association of long term change in the weight, height and surface roughness (Ra) of the above-mentioned materials, aided with SEM observation.

CHAPTER II: LITERATURE REVIEW

2.1. Conventional RMGIC (Vitremer™ Tri-Cure Glass Ionomer System)

Vitremer is an aesthetic, tooth colored, RMGIC restoration which has been used widely in pediatric dentistry since its inception in 1991 (3M ESPE, 2012; Francois *et al*., 2020). It is advantageous for direct chemical adhesion to the tooth structure. This adhesion is aided through the use of adhesive (primer) and this could take place even in the absence of light (3M ESPE, 2012). Vitremer has further advantages of good fracture toughness, moisture tolerance, bulk placement as well as of the release of fluoride and therefore is considered a good choice of restorative material for the high caries risk patients (3M ESPE, 2012; Webman *et al.,* 2016).

Vitremer has been used widely in preventive and restorative dentistry. In preventive dentistry, Vitremer is used as a fissure sealant for primary teeth of children with high caries risk (Provenzano *et al.*, 2010). Likewise, in restorative dentistry, Vitremer is used to restore class I, II, III and V cavities in primary teeth (Webman *et al.*, 2016). It showed a high success rate (around 93%) when applied to these cavities for a three years period (Croll *et al.*, 2001; 3M ESPE, 2012; Webman *et al.*, 2016; Finucane, 2019). There is a moderate evidence to support the use of Vitremer in class II cavities in primary teeth. Furthermore, Vitremer has shown to have higher longevity than conventional GICs when applied to class II cavities in primary teeth (Webman *et al.*, 2016; Finucane, 2019). The application of Vitremer prevents secondary caries at the margin of the restoration and enhances re-mineralization on adjacent proximal caries when placed in 2 mm layers (Croll *et al.*, 2001). On the other hand, for the permanent teeth, Vitremer could be used as an aesthetic restoration for class III and V Cavities, or in cases of non-bacterial tooth loss (3M ESPE, 2012). In addition, it could be used as a temporary restoration for fractured teeth (3M ESPE, 2012; Webman *et al.*, 2016). Moreover, it could be used as a bulk filling material, or for filling of crown preparation defects (3M ESPE, 2012; Webman *et al.,* 2016). Furthermore, Vitremer could be

applied as a 2 mm base material when doing the sandwich technique (Friedl *et al*., 1997; Francois *et al*., 2020). Yet, this usage is only applicable when the pulpal roof of the tooth structure is thicker than 2 mm to avoid diffusion of cytotoxic elements; HEMA or TEGDMA to the pulp tissue (Stanislawski *et al.*, 1999).

However, Vitremer has some limitations. Some of the limitations are related to the RMGICs group such as low wear resistance, brittleness and relatively low strength values (Cattani-Lorente *et al.*, 1994). Other additional limitations could be related to the possibility of incorrect handling from the manufacturer due to the depth of cure with the curing unit being 2 mm (3M ESPE, 2012). Furthermore, the acid base reaction or dark curing is too slow. Therefore, during the maturation phase, dissolution of the cervical proximal box could result in microleakage (Van Dijken *et al*., 1999; Fourie, 2008). Vitremer used in the present study is shown in **Figure (2.1)**.

Figure (2.1): Vitremer material that was used in the present study.

2.1.1. Manipulation

The manufacturer recommends the mixing of Vitremer in standard powder to liquid ratio of (2.5:1) to ensure the best mechanical properties (3M ESPE, 2012). Moreover, the manufacturer advises incremental mixing using a cement spatula for 45 seconds to 3

minutes (3M ESPE, 2012). Use of a syringe system facilitates the placement of the mixed restorative material (3M ESPE, 2012).

2.1.2. Setting reaction

Vitremer is a tri-cured material due to the occurrence of three types of setting reactions in this material (3M ESPE, 2012; Francois *et al*., 2020). Firstly, an acid base reaction occurs between the fluoroaluminosilicate glass and carboxylic group of polyacrylic acid (3M ESPE, 2012; Francois *et al*., 2020). Secondly, the following reaction is the photo-polymerization reaction, which refers to the polymerization methacrylate group of the HEMA component through light activated free radicals as shown in **Figure (2.2)** (3M ESPE, 2012; Francois *et al*., 2020). Furthermore, in the polymerization reaction some of the carboxylic group is substituted by the methacrylate group that is connected through a carbon-carbon double bond (Francois *et al*., 2020). This bond will allow improvement in the polymerization reaction by enhancing the cross-linking between the resin and the polyacid backbone (Francois *et al*., 2020). This second reaction is considered shorter than the first acid base reaction (3M ESPE, 2012). Consequently, the setting time of Vitremer is considered shorter than the conventional GICs (3M ESPE, 2012). Thirdly, the last reaction is the dark cure reaction which includes reaction of the methacrylate group of the polymer system (3M ESPE, 2012). This reaction is considered an additional reaction to provide curing for the areas that are not accessible (3M ESPE, 2012). Some authors argue that this reaction is a polymerization reaction hence; the material has a dual cure setting mechanism. The manufacturers advise light-curing the material up to 40 seconds (3M ESPE, 2012).

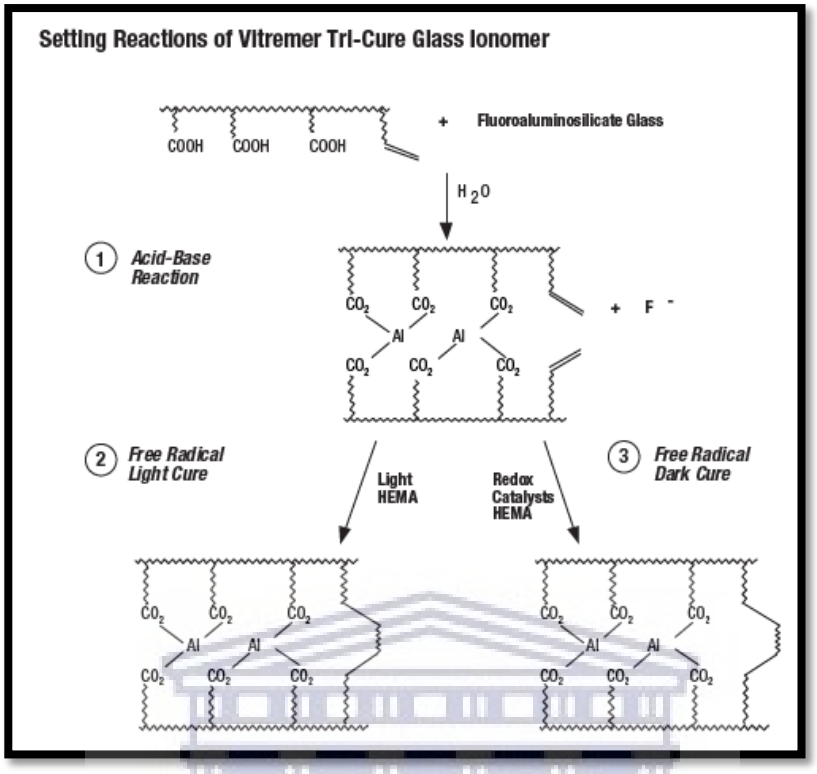


Figure (2.2): Summary of the three setting mechanism of Vitremer from the manufacturer instructions (3M ESPE, 2012).

2.1.3. Vitremer, is it a bioactive material?

The materials, in general, could be classified according to their interaction with the environment as bioactive, bio-inert and bio-responsive (Hench, 1998; Badami & Ahuja, 2014). The term bioactive material was first proposed by Hench (1996). Bioactivity is a biological response at the interface of the material which results in good bond formation (Asthana & Bhargava, 2014). Bioactive materials can be subdivided into *osteo-productive (class A),* which forms bone at the interface and *osteo-conductive (class B)*, which is able to form biocompatible crystals at the interface such as hydroxyapatite (Asthana & Bhargava, 2014). Hydroxyapatite usually reacts with the damaged collagen in the hard tissues and plays a role in cellular differentiation and excretion of the matrix (Abbasi *et al.*, 2015).

The early concepts for the use of materials suggest that the best material to be used in the human body is the inert material that produces minimal tissue response (Hench,

1998). However, there is a paradigm shift in material science from the early concept into the more recent one which gives more preference to ‘‘active’’ materials rather than ‘‘passive’’ ones (Badami & Ahuja, 2014; Abbasi *et al.*, 2015). This new concept usually combines the benefits of releasing ions that interact with hard and soft tissues (Badami & Ahuja, 2014; Abbasi *et al.*, 2015). The bioactivity increases when the amount of calcium in the material increases (Abbasi *et al.*, 2015). Calcium is usually responsible for the formation of the chemical bond between the material and tooth substrate (Abbasi *et al.*, 2015). This will lead to the formation of hydroxyapatite in the presence of phosphate and hydroxide ions (Abbasi *et al.,* 2015). Consequently, a rise in the pH would result in the subsequent destruction of microorganisms (Abbasi *et al.*, 2015). Some of the authors used the term ‘‘smart’’ to describe the bioactive materials (Badami & Ahuja, 2014; Khan *et al.*, 2019). However, others mentioned that the intelligence of the material is related to their behavior in the oral environment, such as their dimensional change in responses to temperature and change in pH when subjected to acidic challenges (Badami & Ahuja, 2014). However, this description of the characteristics of the smart materials varied between many authors in the literature.

There is controversy in the literature whether Vitremer is a bioactive material or not (Banon *et al.*, 2018; Francois *et al*., 2020). Francois *et al*. (2020) noted that all RMGIC materials are bioactive materials. The reason behind this grouping could be due to their ability to induce re-mineralization of the dental tissues through the exchange of the ions (Croll & Nicholson, 2002; Francois *et al*., 2020). On the other hand, Banon and Luc Martin (2018) concluded that all RMGICs are not considered bioactive materials due to the release of very small quantities of calcium and phosphate (Banon *et al.*, 2018).

2.1.4. Dimensional weight changes of Vitremer when immersed in different media

Vitremer, like the rest of RMGICs, is a water-based material as water plays a role in acid base reaction (Miyazaki *et al.*, 1996). Water uptake could be influenced by porosity, and could be affected by the presence of stress due to polymerization shrinkage or a hydro-gel layer around the fillers (Fano *et al*., 2004). The amount of water sorption of Vitremer is also affected by the storage media, such as, acidic media (Nicholson *et al.*,

1999; Şahmalı *et al*., 2003), saliva media (Kanchanavasita *et al*., 1997; Aliping-McKenzie *et al*., 2003; Farias *et al.*, 2018) or water (Yap, 1996; Cattani-Lorente *et al.*, 1999; Emamieh *et al.*, 2011). There are several circumstances in which water could pass through the restoration in different ways such as: 1) during setting, 2) when the material functions inside the oral cavity, or 3) through the diffusion of water from dentin (Jevnikar *et al.*, 2000). This absorption could lead to changes in the dimensions of Vitremer (Fano *et al*., 2004; Emamieh *et al.*, 2011). In the early period of immersion, changes in dimension are usually due to the initial rapid sorption process (Kanchanavasita *et al*., 1997; Nicholson, 1997). After that, there is a balance between water sorption and material degradation (Kanchanavasita *et al*., 1997). It is important to mention that changes in the dimension of any material are time and material dependent. Hence, each material product should be studied separately.

The evidence of water sorption of Vitremer is extensive and conflicting (Kanchanavasita *et al*., 1997; Nicolson, 1997; Iwami *et al.*, 1998; Nicholson *et al*., 1999; Akashi *et al.,* 1999; Cattani-Lorente *et al*., 1999; Aliping-McKenzie *et al*., 2003; Şahmalı *et al*., 2003; Toledano *et al.,* 2003; Fano *et al*., 2004; Emamieh, Ghasemi *et al*., 2011; Farias *et al.,* 2018). This could be related to different immersion periods, the storage media used and wide methodological variations in these studies.

2.1.5. Surface roughness (Ra) of Vitremer

Determination of the surface roughness in the oral environment is complex and difficult to simulate in *in vitro* studies since it is solution and material dependent (Hamouda, 2011; Kazak *et al.*, 2020). Dental wear of Vitremer is affected by two factors; patient factors and restoration factors (Amaechi & Higham, 2005). Due to the fact that this study was conducted *in vitro*, a review about the effect of material factors on the Ra of the Vitremer is discussed below. While literature on this topic is abundant and extensive, research on Activa or Cention N is lacking. Consequently, in this dissertation, these factors that control the Ra are reviewed based on Vitremer literature as follows:

- **The composition**

Resin and matrix compositions and consequent types of setting reactions mentioned above will affect the hydrolytic stability and hence the roughness of Vitremer material (Paula *et al*., 2011). Furthermore, Kazak *et al.* (2020) mentioned that there is a direct relationship between the wear pathway and the composition of the dental material.

- **Filler characteristics and their effect on the degree of conversion**

The size, chemical compositions, shape and surface treatment of the fillers, hydrophilic nature of the monomer and the polymerization process have a role in the total wear of any dental material (Erdemir *et al.*, 2013; Rodrigues *et al*., 2015; Osorio *et al.*, 2016; Kazak *et al.*, 2020; Kumar *et al*., 2020). Regarding the size of Vitremer particles, the smaller the particles, the lesser the surface roughness values and hence the wear (Beresescu *et al.,* 2015; Rodrigues *et al*., 2015; Osorio *et al.,* 2016). This is due to the fact that the smaller the particle, the lesser the vertical dimensions (Osorio *et al.*, 2016). Consequently, this will lead to a higher probability for adherence to the resin matrix which is presented clinically by smooth surfaces (Osorio *et al.*, 2016). Pedrini *et al*. (2003) found that Vitremer had a higher Ra mean (0.397 µm) than compomer (Dyract) (0.27 µm) and lower than Chelon-Fill conventional GICs (0.53 µm) when the same soflex discs were used for the three materials for a period of one week. This intermediate level of Ra is due to equal distribution of the small and large elements of the RMGICs (Gladys 1997; Pedrini *et al*., 2003). The same study showed that the surface characteristics were not affected by the immediate finishing and polishing, up to one week after placement of the restoration (Pedrini *et al.*, 2003). Giving more focus to the relation between filler size and the degree of conversion, it has been proven that the smaller the particle, the higher the degree of conversion of the monomer into polymer (Rodrigues *et al*., 2015). However, the degree of conversion of Vitremer is further influenced by the resin matrix and the composition of the fillers (Palmer *et al.*, 1999; Kim *et al.*, 2015).

- **The powder to liquid ratio (PLR) of the cement**

Reduction of the wear resistance is found to be associated with a reduction in the powder: liquid ratios during the mixing of the cement (Beresescu *et al.*, 2015). This fact has been linked to the reduction in the ratio of the glass particles in the powder that made the cement less resistant to wear (Beresescu *et al.*, 2015). Lower wear resistance equates to an increased surface roughness (Ra) of Vitremer (Rodrigues *et al*., 2015). Consequently, this will lead to a shift in the inorganic particles and thus a higher probability of the incorporation of air during the preparation of the final cement (Beresescu *et al.*, 2015; Rodrigues *et al*., 2015). Rodrigues *et al*. (2015) revealed that incorporation of air bubbles leads to an increase in surface roughness of Vitremer.

- **Quality of the finishing and polishing of the final restoration**

High-quality finishing of the surface of any restoration is important for retention of the restoration, preservation of the natural color of the restoration as well as patient comfort (Koupis *et al.*, 2007; Beresescu *et al.*, 2015). Finishing and polishing procedures are independent and there is a kind of ambiguity between them (Koupis *et al.*, 2007). Finishing (shaping) means contouring of the restoration in order to provide the desired anatomy (Koupis *et al.*, 2007; Erdemir *et al.*, 2013). On the other hand, polishing means reduction of the rough scratches that could be created by the finishing instruments (Koupis *et al.*, 2007; Erdemir *et al.*, 2013). The polishing system had been shown to affect the surface characteristics of tooth colored restorations (Erdemir *et al.*, 2013). In particular, finishing and polishing could determine the final roughness of the surface of the restoration through many parameters, such as; the flexibility of the finishing material, the hardness of the abrasive used the method of application of the instruments and the grit size (Erdemir *et al.*, 2013).

When considering the finishing and polishing factor, it is important to note three factors in order to get the smoothest surface of the restoration. Firstly, *the instruments that are used in the finishing procedure*, such as abrasive strips and disks, rubber cups and points (Hondrum & Fernandez,1997; Wilder *et al.*, 2000; Koupis *et al.*, 2007; Erdemir *et al.*, 2013). However, no consensus had been provided regarding the best polishing system that gives the best finishing and polishing (Hayacibara *et al.*, 2004; Koupis *et al.*,

2007). Scholars agree that the smoothest surface could be obtained with the Mylar strip (Hondrum & Fernandez, 1997; Pedrini *et al.*, 2003; Erdemir *et al.*, 2013). However, when abrasive papers are used, the hardness of the abrasive used and the grit size would play a significant role in the quality of the final surface of the restorative material (Erdemir *et al.*, 2013). It is important to mention that abrasive particles must be harder than the restorative material in order to remove the rough and large, un-reacted filler from the surface of the material (Erdemir *et al.*, 2013). Yet, little information is available in the literature regarding the finishing and polishing of the RMGICs.

Secondly, the *timing of finishing and polishing* is considered critical to gain the best properties of the final cement. Therefore, it is important to delay the finishing until the material has matured completely (Hayacibara *et al.*, 2004; Koupis *et al.*, 2007). Delaying of the polishing provides a smoother surface when compared to immediate finishing and polishing (Koupis *et al.*, 2007). However, the literature is inconclusive about the exact time required before starting the finishing and polishing.

Thirdly, *the method of finishing and polishing is also a factor* to consider. Many methods have been mentioned in the literature on acceptable finishing, but the most recommended one is the circular planar motion (Koupis *et al.*, 2007). The argument in the literature is whether dry or wet polishing is the best for the RMGICs (Wilder *et al.*, 2000; Erdemir *et al.*, 2013). While dry polishing has been reported to provide good topography and could enhance the strength, some authors recommend wet polishing in order to reduce the temperature of the cement, avoid the desiccation of the glass ionomer cement and hence prevent weakening of the mechanical properties of the RMGICs (Wilder *et al.*, 2000; Koupis *et al.*, 2007; Erdemir *et al.*, 2013).

Nevertheless, it is difficult to provide a smooth surface for the tooth colored restorative materials after polishing due to the fact that the final outcome depends on the material properties combined with three full parameters in order to get the optimal results. Each material is different in terms of size, shape and ratios of the filler materials to the chemical content (Erdemir *et al.*, 2013). In particular, a proportional relationship between the size of the particles and the Ra values was found; the larger the particles, the rougher the surface (Erdemir *et al.*, 2013). Furthermore, when the filler ratio of the

amount of the filler is very small, this would result in higher capabilities of the larger filler to dislodge during the polishing (Erdemir *et al.*, 2013). Furthermore, polishing should be done according to the manufacturer's instructions.

The assessment of the roughness of the material after finishing can be done in three ways; clinically, by visual evaluation of the final surface, microscopically, with the use of the scanning electron microscope or analytically, with the use of pro-filometric analysis (Koupis *et al.*, 2007). The last mentioned method was used in the present study which includes quantitative measurement of specific values in order to determine the final roughness of the material after finishing and polishing of the restorative material (Koupis *et al.*, 2007). Every method mentioned has its advantages and disadvantages, and it is not advisable to rely on a single method in the assessment of the restorative material to avoid misleading results (Koupis *et al.*, 2007). Literature regarding the finishing and polishing of the newer materials such as Cention N and Activa is lacking currently.

- **Effect of the storage media on the surface roughness of Vitremer**

Mechanical properties of Vitremer are not only affected by the mechanical compositions and the material characteristics, but are also affected by the environment to which they are exposed whether acid media (De Gee *et al.*, 1996; Fano *et al*., 2004; Fucio *et al*., 2008; Honorio *et al*., 2008; Briso *et al.,* 2011; Hamoda., 2011; Correr *et al*., 2012; Carvalho *et al*., 2012; Paula *et al*.,2014) saliva media (Yip *et al.,* 2004; Honorio *et al*., 2008; Beresescu *et al.,* 2011; Paula *et al*., 2014; Beresescu *et al.,* 2015).

2.2. New bioactive materials

There is variation in the wear resistance between different tooth-colored restorative materials. This could be presented by a continuum indicating the highest to the lowest resistant material to wear (Hamouda, 2011; Rodrigues *et al*., 2015). Composite restorations have the best wear resistance followed by compomer, RMGICs and then finally the conventional GICs (Şahmalı*, et al.*, 2003; Honório *et al.*, 2008; Hamouda, 2011; Rodrigues *et al*., 2015). Composite is considered the best material in terms of resistance to wear and this could usually be linked to the presence of the saline coupling agent (Hamouda, 2011). On the other hand, conventional GICs was found to

be the least resistant to surface wear (Yip *et al.,* 2004; Hamouda, 2011), due to the larger particle size of conventional GICs and the fact that it has more water sensitivity than other materials (Hamouda, 2011). Furthermore, the mean size of the voids and fillers was the largest in the conventional GICs, followed by the RMGICs while the least voids and smallest size of the filler was found in the composite resin (Yip *et al.*, 2004).

Recently, one of the aims in the development of bioactive materials such as Activa and Cention N is to buffer the acidic media environment through the incorporation of certain types of fillers that release a large amount of ions (Activa Bioactive, 2016; Todd, 2016; Cention N, 2018). Some authors claim that adding bioactive particles to the polymer could alter the degradation rate of the material due to their direct effect on the hydrophilicity, sorption properties, final weight of the material and the pH (Osorio *et al.*, 2016).

2.2.1. Activa Bioactive Restorative

Activa bioactive restorative **Figure (2.3)** (Pulpdent, Watertown, MA, USA) is a new restorative material (Bansal *et al.*, 2016; Banon, 2018). It was developed after the Pulpdent Company received approval from the Food and Drug Administration (FDA) (FDA report, 2012). Activa was introduced to the market for the purpose of making use of the benefits from both GICs and resin based composite as well as eliminating their drawbacks (FDA report, 2012; Croll *et al.*, 2015; Banon, 2018; Owens *et al.*, 2018). Therefore, the material claimed to have a combination of strength and moisture tolerance, chemical adhesion, and release and recharge of ions (Amaireh *et al.*, 2019), aesthetics of the composite resin and the advantages of the GICs in terms of tolerance (Bhadra *et al.*, 2019).

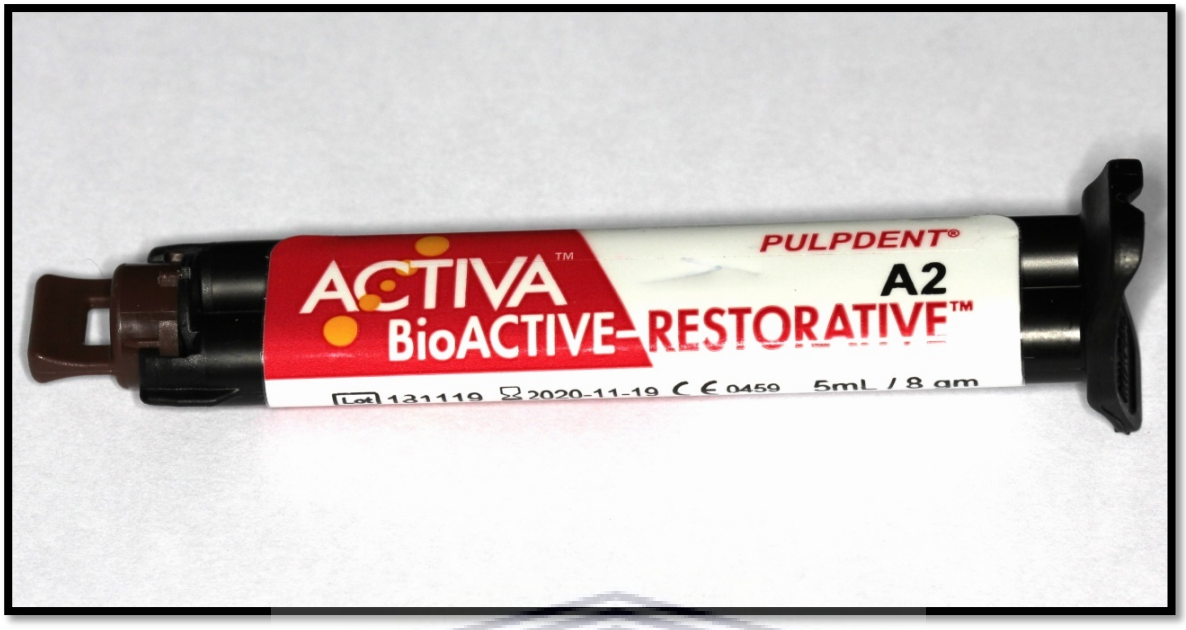


Figure (2.3): Activa Bioactive restorative material used in the study.

The manufacturer considered Activa as a bioactive and biocompatible material. Bioactivity means the capacity of the material to have an effect on the living tissue and exhibit some bioactive fixation due to its reaction with human tissue (Porenczuk *et al.*, 2019). Activa was claimed to be "bioactive" because it is hydrophilic, shock-absorbing, rubberized and has a bioactive resin matrix (also called Embrace ionic resin) in addition to bioactive fillers that release ions such as calcium and fluoride (Zhang *et al.,* 2017; Banon, 2018; Owens *et al.*, 2018; Benetti *et al.*, 2019; Van Dijken *et al.*, 2019). Recent literature showed that Activa releases phosphate as well (Tiskaya *et al*., 2019; Ruengrungsom *et al*., 2020). The release of ions from Activa was claimed to protect against leakage and has anti-bacterial properties as well (Zhang et *al.*, 2017). The bioactivity of this material is due to its ability to form hydroxyapatite at the restoration interface, which takes place when saliva interacts with the ions of the restoration (Amaireh *et al.*, 2019). However, Porenczuk *et al.* (2019) claimed that the bioactivity of this material is mainly due to the presence of the bioglass SiO_2-CaO-Na_2O-P_2O_5. The material releases fluoride in the form of YbF_3 but the amount of fluoride that is released from this filler is very scanty and not enough to ensure re-mineralization of the tooth *per*

se (Porenczuk *et al.,* 2019). In fact, the exact chemical structure and chemical setting reaction was not mentioned in the manufacturer's instructions (Activa Bioactive, 2016).

Activa is also declared as "biocompatible" because it is free from bisphenol A, Bis-GMA and BPA that usually have toxic effects on living tissues (ElReash *et al.*, 2019; López-García *et al.*, 2019; Porenczuk *et al.*, 2019). The absence of these components could play a role in improving the mechanical properties through reduction of the viscosity and rigidity of this new material (Alrahlah, 2018). Although some clinical trials have been published on this material, literature is very scarce on Activa and more clinical long term studies are still required.

2.2.1.1. Manipulation and setting reaction

Activa is an injectable paste-paste system in an automix syringe (Croll *et al.*, 2015; Banon, 2018). However, it is important to be careful to avoid air bubbles during dispensing (Croll *et al.*, 2015). As mentioned on the material safety data sheet, the first paste consists of: diurethane dimethacrylate and other methacrylate-based monomers, oligomers, polyacrylic acid/maleic acid copolymer, water, barium borosilicate glass, silica, reducing agents and a photo-initiator (FDA report, 2012). The second paste is composed of: diurethane dimethacrylate and other methacrylate based monomers and oligomers, aluminoflurosilicate ionomer glass, silica and oxidizing agents (FDA report, 2012). The resin monomer that is added to the material was claimed to improve the wear and resilience properties (Van Dijken *et al.*, 2019). The material safety data sheet illustrates that the material has methyl methacrylate components and sodium fluoride particles, while the types of monomer were not mentioned. Furthermore, no information about the particle size, filler loading or filler percentage was provided.

When considering the setting reaction of Activa, it is important to mention that Activa is a tri-cured material (FDA report, 2012; Croll *et al.*, 2015; Banon, 2018). This is based on the fact that it has three setting mechanisms; self-cure, light-cure of the resin and a chemical cure mechanism (FDA report, 2012; Croll *et al.*, 2015; Banon, 2018). The self-cure reaction includes the acid base reaction of the GIC and the self-cure reaction of the resin (Banon, 2018). The light-cure reaction improves the mechanical properties through enhancement of the cross-linking of the polymer (Banon, 2018). This tri-cure

property would give the clinician an advantage especially in a situation where the light-cure does not penetrate properly and the material will consequently continue setting through the chemical curing until it is completely set (Croll *et al.*, 2015).

2.2.1.2. Mechanical properties

As claimed by the manufacturer, Activa has very good mechanical properties. One of the important properties of Activa is the ability to absorb water; this water sorption may jeopardize the bioactivity but does not affect the physical properties (Banon, 2018; ElReash *et al.*, 2019). The literature is lacking regarding the water sorption of Activa. The other claimed physical property is related to its ability to release a constant amount of fluoride without re-charging (Banon, 2018). Furthermore, there is some evidence that Activa releases a lesser amount of fluoride in comparison to conventional GICs such as Fuji IX and Equia Forte (GC products) (Banon, 2018).

2.2.1.3. Activa, a RMGIC or composite?

There are controversies in the literature whether Activa is a RMGIC or a resin based composite (Bansal *et al.*, 2016; Banon, 2018). Some authors categorize Activa as a RMGIC (FDA report, 2012; Croll *et al.*, 2015; Pameijer *et al.,* 2015; Alrahlah, 2018; Banon, 2018). The reasons for grouping it as RMGICs could be attributed to the presence of two acids: polyacrylic and maleic acid in its compositions (FDA report, 2012; Croll *et al.*, 2015; Pameijer *et al.,* 2015; Alrahlah, 2018; Banon, 2018). On the other hand, some authors believe that Activa is an "ionic" resin composite due to the fact that the chemical cure is combined with the self-curing property of the resin composite (Banon, 2018; ElReash *et al.*, 2019). The term "ionic" here refers to the ionization process of a phosphate group that is located between the resin and filler on one side which binds to the tooth structure on the other side (Banon, 2018). The ionic bond is formed when the hydrogen bond of the organic molecule that incorporates the phosphate atom is replaced by calcium when binding to the tooth structure as shown in **Figure (2.4).**

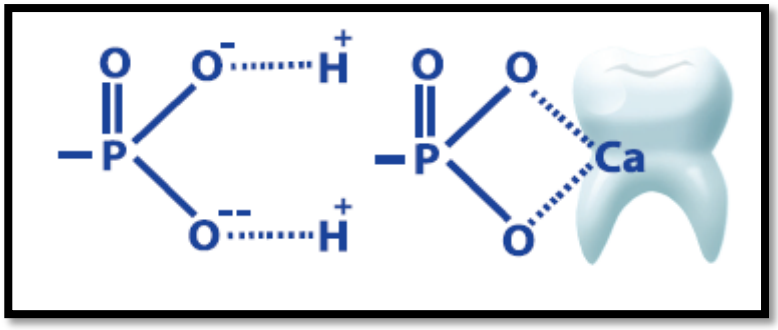


Figure (2.4): Ionic bond formation due to the replacement of hydrogen bond with calcium.

However, in order to decide, a person must look at the general characteristics of RMGICs to apply these criteria critically to Activa. Any material that is classified as RMGICs should fulfill the following requirements:

- **The material should contain all the components necessary for an acid base reaction** (the glass, polymeric acid or modified polymeric acid and sufficient quantity of water) to allow for the acid base reaction. This reaction is considered a significant determinant for categorising any glass ionomer material (Sidhu & Watson, 1995; Nicholson & Czarnecka, 2009). This is clinically reflected by the ability of the material to set in the dark (Sidhu & Watson, 1995). However, it is controversial whether the material that gives an acid base reaction over a period of months could be considered true glass ionomer cement (Sidhu & Watson, 1995; Kakaboura, *et al.*, 1996).
- **The material should have at least a dual cure setting**: chemical curing (or the acid base reaction) in addition to the light curing (Sidhu & Watson, 1995; Nicholson & Czarnecka, 2009). A free radical or photo polymerization reaction of the water soluble resin material such as HEMA or Bis-GMA is considered critical for setting of RMGICs (Sidhu & Watson, 1995; Nicholson & Czarnecka, 2009).
- **At least one polymerization initiator system that is chosen from a group should consist of a photo-initiator system, an alkali aromatic sulfinate or any combination between them** (Sidhu & Watson, 1995; Nicholson & Czarnecka, 2009; Qian *et al.*, 2016).

- **Chemical adhesion to tooth structure and continuous fluoride release** (Sidhu & Watson, 1995).

When these criteria were applied to Activa the following were found: Activa contained modified polyacrylic acid as mentioned in the material safety data sheet. However, the presence of the photo-initiator was not clear. Furthermore, the manufacturer did not provide any information about the chemical composition of the material.

Regarding the setting reaction, Activa has a triple cure setting mechanism: chemical acid base reaction, photo polymerization reaction and self-cure resin polymerization. However, the chemical equation of setting reactions was not discussed by the manufacturer. Therefore, the reaction could involve an acid base reaction according to the Brønsted-Lowry acid base theory. The Brønsted-Lowry acid base theory defines the acid as a compound that is capable of donating a proton, and a base as a chemical compound that is capable of accepting that proton. i.e.: the base requires one pair of electrons in order to make a bond with the proton (Sun & Silverman, 1945; Vogler, 1998). On the other hand, Lewis divides the chemical reactants into the acid and bases according to their tendency to donate one or more pairs of electrons and their power capability to accept one or more pairs of electrons respectively (Vogler, 1998; Das et *al.*, 2013). Hence, the reaction could not be explained through the Lewis acid base theory due to the lack of information about these chemical reactions.

As claimed by the manufacturer, Activa has the ability to adhere chemically to the tooth structure, as well as a fluoride-releasing ability.

In essence, it could be concluded that Activa is a RMGIC that releases bioactive ions. Most of the studies in the literature on Activa were focused on flexural strength and micro-leakage. Literature is lacking on the long-term wear of Activa in relation to other RMGICs.

2.2.2. Cention N

Cention N was introduced to the market as a "bioactive" material and as an alternative to amalgam (Deepak & Nivedhitha, 2017; Samanta *et al.*, 2017; Van Ende *et al*., 2017). The manufacturer claims that this material has many advantages such as relative

aesthetics, acceptable handling properties, short setting time, ability to release fluoride and therefore could help in the re-mineralization of the cavity (Todd, 2016). In addition, the material has a dual cure setting mechanism through the self-cure and additional optional light curing properties (Todd, 2016; Deepak & Nivedhitha, 2017). Although the manufacturers state that the material could be used safely without adhesive, they still recommended the use of adhesive for the best results (Todd, 2016; Van Ende *et al.*, 2017). Thus, it allows fast application especially when dealing with children (Deepak & Nivedhitha, 2017). Some authors have predicted that Cention N will have a promising future in restorative dentistry as it is cost-effective for both the patient and the dentist (Deepak & Nivedhitha, 2017). In particular, Cention N could be used for restoring the primary and permanent teeth especially class I, II and V (Todd, 2016; Deepak & Nivedhitha, 2017). Furthermore, Cention N can be used as a barrier material in root canal treated teeth (Pandey *et al*., 2018). The manufacturer only recommended the use of retentive preparation in a manner similar to amalgam restoration (Todd, 2016). **Table (2.1)** below shows the difference between the manufacturers' claims for the materials used in the present study.

Table (2.1): Illustrates manufacturers' claims for the materials included in the study.

Advantages and clinical use	Vitremer	Activa	Cention N
Aesthetics	✓ Not long term	✓	✓
Good handling properties	no	✓	✓
Compulsory command set	✓	✓	✓
Tolerance to moisture	✓	✓	Unknown
Chemical adhesion	✓	✓	bonding agent required

Fluoride release	✓	✓	✓
Calcium release	✓	✓	✓
Phosphate release	unknown	✓	unknown
Usage as a bulk fill	✓	Unknown	✓
Restoration of primary teeth	✓	✓	✓
Restoration of the permanent teeth	✓	✓	✓ Especially (Class I,II and V)
Additional mechanical retention is needed during cavity preparation	no	no	✓
Bioactivity	✓	✓	✓

2.2.2.1. Manipulation and setting reaction

Cention N is available in liquid and powder form as shown in **Figure (2.5)**. The manufacturer claims that the use of the correct powder to liquid ratio (4.6:1) will ensure good strength of the final restoration (Todd, 2016; Cention N, 2018). This is equivalent to one scoop of the powder and one drop of liquid. The manufacturer recommended the preparation of the cavity to an outline of at least 1.5 mm depth and width (Todd, 2016; Cention N, 2018). Furthermore, the manufacturer recommended light curing between 20 - 40 seconds if used.

Figure (2.5): Cention N that has been used in the study.

The powder contains the organic part while the liquid contains the inorganic part (Todd, 2016; Cention N, 2018). As claimed by the manufacturer, *the powder or the organic part* consists of the following fillers;

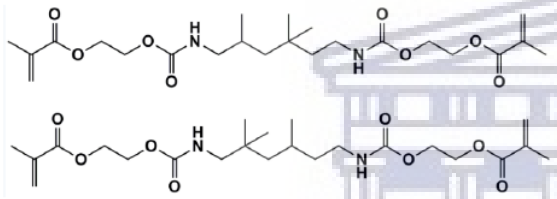
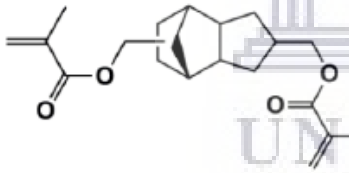
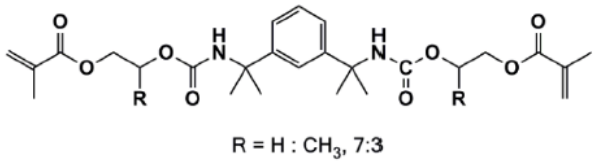
- **Barium aluminium silicate glass:** enhances the strength of Cention N.
- **Aluminium tri-fluoride.**
- **Ytterbium tri-fluoride**: to make the material radio-opaque.
- **Technology Iso fillers (Tetric N- Ceram):** Reduces the contraction stress of the material during the polymerization shrinkage.
- **Calcium barium aluminium fluorosilicate glass filler.**
- **Calcium fluorosilicate (alkaline) glass filler:** The main function of the alkaline fillers is to enhance the release of hydroxide ions and hence act as a buffer when the pH drops during the acidic attack (Todd, 2016). The alkaline fillers are claimed to be "bioactive" due to the release of calcium, phosphate and fluoride that play a role in the re-mineralization of the affected dentin (Todd, 2016; Deepak & Nivedhitha, 2017; Van Ende *et al*., 2017; Tiskaya *et al*., 2019). It is important to mention that the presence of calcium and a phosphate in any product would provide re-mineralization to the tooth surfaces especially when a

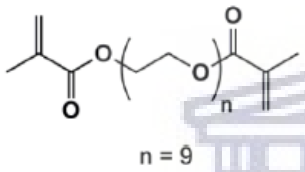
significant amount of fluoride is also provided (Koch, 2017; Wellbury, 2018). Recent elemental analysis by Ruengrungsom *et al*. (2020) confirms that calcium, phosphate and fluoride were present in Cention N. Another idea behind the development of the reactive fillers is to reduce the chances of secondary caries, particularly when the bioactive materials are released into the tooth- restoration interface (Tiskaya *et al*., 2019). This situation is noteworthy due to the fact that any material that sets by a polymerization reaction will exhibit a marginal gap and therefore, have higher a propensity to secondary caries (Tiskaya *et al*., 2019).

The size of Cention N fillers ranges from 0.1 µm to 35 µm (Todd, 2016). The smallest size of the particles is equal to 100 nanometers. Consequently, more accurate investigation is needed to confirm if the material contains nano-fillers or not. This is due to the fact that nano-technology is the production of functional materials ranging from 0.1 to 100 nanometers (Hedge *et al.*, 2008). Moreover, it is important to mention that the manufacturer claimed that all the fillers receive treatment to the surface (except Ytterbium tri-fluoride) in order to get enough moisture from the liquid and hence adapt well to the polymer matrix (Todd, 2016). However, this point needs further research for validation.

Alternatively, the *inorganic part that usually forms the liquid* is composed of four monomers which form the matrix (Todd, 2016). The monomers usually represent 12 - 40% of the final material (Todd, 2016). The four monomers are mentioned in the following **Table (2.2).**

Table (2.2): The chemical formulae of the organic monomers that form the liquid part of Cention N (Todd, 2016).

Monomer	Chemical formula	Description
(UDMA) Urethane di-methacrylate		Hydrophobic monomer, forms the main component of the matrix
(DCP) Tricyclodecan-dimethanol dimethacrylate		Difunctional low viscosity monomer, has an aliphatic, aromatic backbone
(Aromatic aliphatic-UDMA): Tetramethyl-xylylen-diurethane		Stiff compound, decreases the chances of discoloration through the combination between its aliphatic aromatic part

dimethacrylate		
(PEG - 400 DMA): Polyethylene glycol 400 di-methacrylate	 n = 9	Hydrophilic monomer, makes the material flowable, provides good moisture to the tooth surface

It is also claimed that during the polymerization, the four monomers cross-link with each other to form a resilient combination with good mechanical properties (Todd, 2016). It is important to mention that Cention N does not contain any Bis-GMA, HEMA, or TEGDMA (Todd, 2016).

2.2.2.2. Cention N, is it an"Alkasite" or RMGIC?

The grouping of Cention N as a dental material is a topic of controversy in the literature. The bulk of the literature categorizes it as an alkasite, a subgroup of compomer resin hence; they are following the manufacturer (Todd, 2016; Cention N, 2018). However, recently Ruengrungsom *et al*. (2020) considered it as a separate new group called "resin based ion leaching materials" (RB - ILM). Ruengrungsom *et al*. (2020) classified Activa in the same group of (RB - ILM) as well. However, some authors such as Tiskaya *et al.* (2019) classify Cention N as a bioactive composite and stated that Cention N had some weak ionomer properties. The reason behind this claim is the presence of ionomer type glass in the SEM (Tiskaya *et al.*, 2019). However, Tiskaya only criticized this information from the SEM without any elemental analysis conducted. In essence, Cention N actually lacks the densely cured structure of the compomer. Furthermore, the powder and liquid packing makes it more in line with RMGIC that releases alkali ions.

Furthermore, certain features differentiate the RMGICs from the composite resin (as mentioned earlier in the Activa bioactive restorative subheading).

In particular, when applying these characteristics to Cention N, it showed that this material could be categorized as a resin-modified glass ionomer material (RMGIC). This could be due to the following:

1. Cention N has a self-curing mechanism (Todd, 2016; Cention N, 2018). The setting reaction is divided into two mechanisms:

- **Radical formation:** through one electron transfer reaction. The process of electron transfer is a multi-stage process and it is a pH dependent step (Kirchnerová & Purdy, 1981). In another way, the reaction took place when Thiourea reacts with other compounds that have a low pH or are acidic (Kirchnerová & Purdy, 1981). This reaction is shown in **Figure (2.6)** below.

- **Oxidation-reduction reaction:** the two parts of the reaction are seen in the **Figure (2.7)** below:

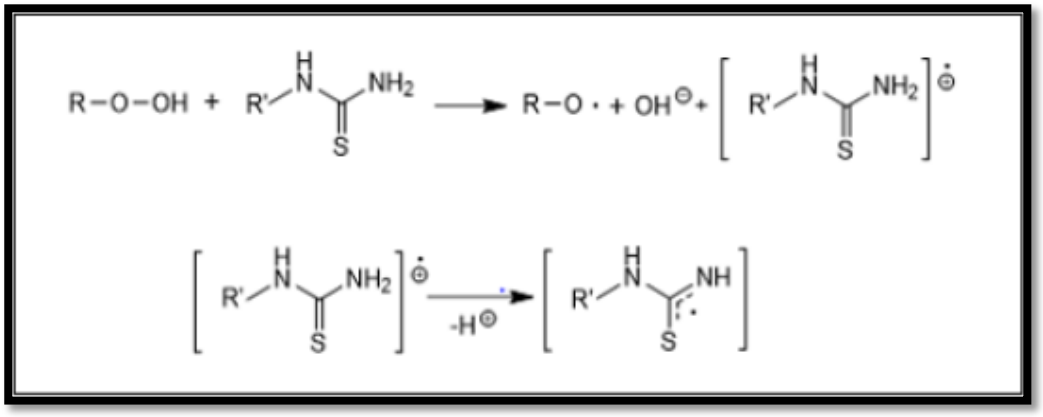


Figure (2.6): The first setting reaction of Cention N which includes radical formation.

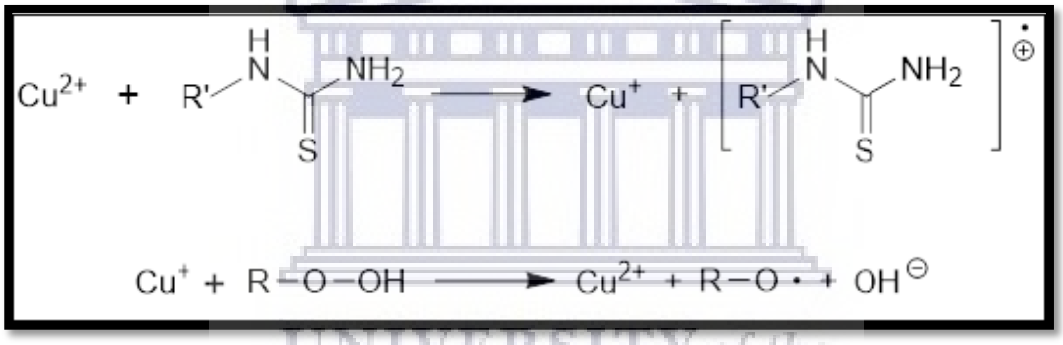


Figure (2.7): The second setting reaction of Cention N, the oxidation reduction reaction.

Thiourea is an organic compound that has a high affinity to react with low pH or acidic compounds (Chesley, 1944; Ushasree *et al.*, 1999). This is due to the fact that any reduction in the pH results in more affinity of the sulphate ions to be introduced for coordination (Ushasree *et al.*, 1999; Sahu *et al*., 2011). Copper salt is the catalyst for the setting reaction (Todd, 2016). The polymerization that takes place here is the radical polymerization type (Todd, 2016).

However, although the auto-curing mechanism is present in Cention N, the type of the setting reaction is debatable in the literature, whether it is a redox reaction or acid base reaction. In particular, when this reaction is considered a redox type reaction, it is classified as an oxidation inhibition or reduction reaction between two organic molecules, namely the hydro-peroxide and Thiourea molecules (Krivenko *et al*., 2003).

Redox reactions are groups of reactions that show transfer of electrons between two molecules in order to form anionic and cationic parts (Das et *al.*, 2013).

Reduction: oxidant + e^- → Products

Oxidation: Reductant→ products + e^-

Although the setting reaction of Cention N could be categorized as a redox reaction, nevertheless, there are two contradicting theories in categorizing this type of reaction: Brønsted-Lowry acid base theory and Lewis acid base theory. The former theory was discussed under Activa subheading.

Lewis's theory on the other hand, which was regarded more modern than the Brønsted-Lowry acid base theory, considers the setting reaction of Cention N as an acid base reaction (Brewer., 1984; Vogler, 1998; Das et *al.*, 2013). Therefore, this definition is a very wide term in describing the acid base reactions. Some authors argue that Lewis's acid base reaction, although it is an inclusive theory, has a limitation in the quantitative interpretation of acid base reactions (Sun & Silverman, 1945). It is clearly seen in the chemical setting reaction of Cention N that there is no loss or acceptance of the proton between the reactants. Hence, this reaction, according to this theory, is not considered an acid base reaction. However, the fundamental difference between the Lewis acid base reaction and redox reaction is that Lewis's reaction requires adduction through co-ordination with a covalent bond (Das *et al.,* 2013). Hence, due to the presence of some ambiguity between the Lewis acid base reaction and the redox group of reactions, Cention N setting reaction could be justified as an acid base reaction according to Lewis's theory of acid and bases. Hence, this justification could approve the manufacturer claim of the manufacturer about the self-curing property of Cention N (Cention N, 2018).

2. Cention N has an Ivocerin photo-initiator as well as an acyl phosphine oxide initiator for optional light curing. This photo-initiator is found in the powder and in a Norrish Type I initiator (Todd, 2016).

3. Information about the method of bonding of Cention N to the tooth structure is lacking in the literature. More experimental and clinical research is needed on this topic.

In conclusion, the existing literature seems to favor Cention N classification as an Alkasite i.e. a resin-based composite with alkaline fillers, as confirmed by the manufacturer. Yet it is similar enough to RMGIC to be included for comparison in this study. This argument is made for the first time in this dissertation, since the three materials are certainly similar in terms of indications for use but vary broadly in their chemical composition.

2.3. Conclusion

The study used two experimental RMGICs and one conventional RMGIC (Vitremer) to study their interactions with neutral artificial saliva and lactic acid solutions for a period of one year. The effect of the pH on these changes was noted. Comparison of these materials and the properties tested enabled the researcher to draw conclusions on the performance of the RMGICs, which would be clinically transferable. The results from these experiments provided insight into the potential longevity of these materials based on the parameters of the study. The rationale for the aforementioned comparison is based on the long clinical success that Vitremer had enjoyed. Therefore, the comparison of the results of Vitremer with Cention N and Activa would be clinically relevant.

CHAPTER III: MATERIALS AND METHODS

A discussion of the materials used and the methodology for this study follows after a description of the aim, objectives and research hypothesis as outlined below:

3.1. Aim

The aim of this study was to compare selected mechanical properties of Cention N, Activa and Vitremer; and to draw conclusions on the effect of artificial saliva and a low pH solution on these materials.

3.2. Objectives

1. To determine the association between the weight (difference in weight in relation to baseline) of each studied material and time of immersion in acid or saliva media for a one-year period.

2. To determine the association between the height (difference in height in relation to baseline) of each studied material and time of immersion in an acid or saliva media for a one-year period.

3. To determine the association between the surface roughness (difference in surface roughness in relation to baseline) of each studied material in relation to the time of immersion in an acid or saliva media for a one-year period.

4. To determine the association between the amount of fluoride that is released into de-ionized water from each of the studied materials for a period of one month.

3.3. Research hypothesis (Null hypothesis)

The null hypothesis for this study assumed that there would be no difference in the selected properties in terms of weight, height and surface roughness of the three materials upon immersion in acidic media or artificial saliva solution for a period of one year and fluoride release into de-ionized water for one month.

3.4. Materials

The materials evaluated comprised of two chemically cured RMGICs: Vitremer (3M ESPE, Paul, MN, USA), Activa (Pulpdent, Watertown, MA, USA) and one alkasite (Cention N, Ivoclar Vivadent, Liechtenstein, Austria). **Table (3.1)** below provides the manufacturer details of the materials studied.

Table (3.1): Compositions of the dental materials that were used in the present study.

Material	Type	Manufacturer	P/L ratio	Composition (Fillers)	Compositions (Matrix)	Mean Particle size	Batch no.	Expiry date
Vitremer	Hand mixed	3M dental products, St Paul, MN, USA	2.5:1	***Powder*:** radio-opaque fluoro-alumino-silicate glass	***Liquid:*** Aqueous, light sensitive solution of modified polyalkenoic acid	3 µm	MA02472	19/11/2020
Activa Bioactive restorative	Auto mix-	Pulpdent; water	1:1	The compositions were not mentioned by the manufacturer. However, according to material safety data sheet the compositions could be ***Fillers:*** silica (6.7%) as inorganic particles, sodium fluoride (0, 75%). Moreover, barium borosilicate glass FDA, 2012).		Not specified	181119	19/11/2020

	two paste system.	town, MA, USA		***Matrix:*** blend of diurethane di-urethane modified with hydrogenated poly-butadiene and methacrylate with modified polyacrylic acid (44.6%); patented rubberized resin (Embrace), water and Camphorquinone (photo-initiator). polyacrylic acid/maleic acid (FDA, 2016).				
Cention N	Hand mix	Ivoclar Vivadent	4.6:1	***Powder:*** Inorganic fillers (Ba-Al-Ca-Ba-Al-F) silicate glass, Ca-F-silicate glass, YbF_3) and customized fillers	***Liquid:*** Urethane dimethacrylate, Tricyclodecan-dimethanol dimethacrylate, polyethylene glycol dimethacrylate	0.1 µm-35 µm	W06917	3/2/2019

3.5. Study design and sample size

In order to address the aforementioned aims and objectives of the present study, a comparative experimental *in vitro* study was performed. The total sample size (n = 60) consisted of three different dental materials; 20 samples of Vitremer (3M ESPE, Paul, MN, USA, lot number: N945953 (liquid), N908909 (powder), 20 of Activa (Pulpdent, Watertown, MA, USA, lot number: 181119) and 20 of Cention N (Ivoclar Vivadent, Liechtenstein, Austria), lot number for powder and liquid; (W06917). Each material (comprising 20 samples each) was divided through the use of simple randomization (n = 10) to be placed in acidic media or artificial saliva (n = 10) as shown in **Figure (3.1)** below.

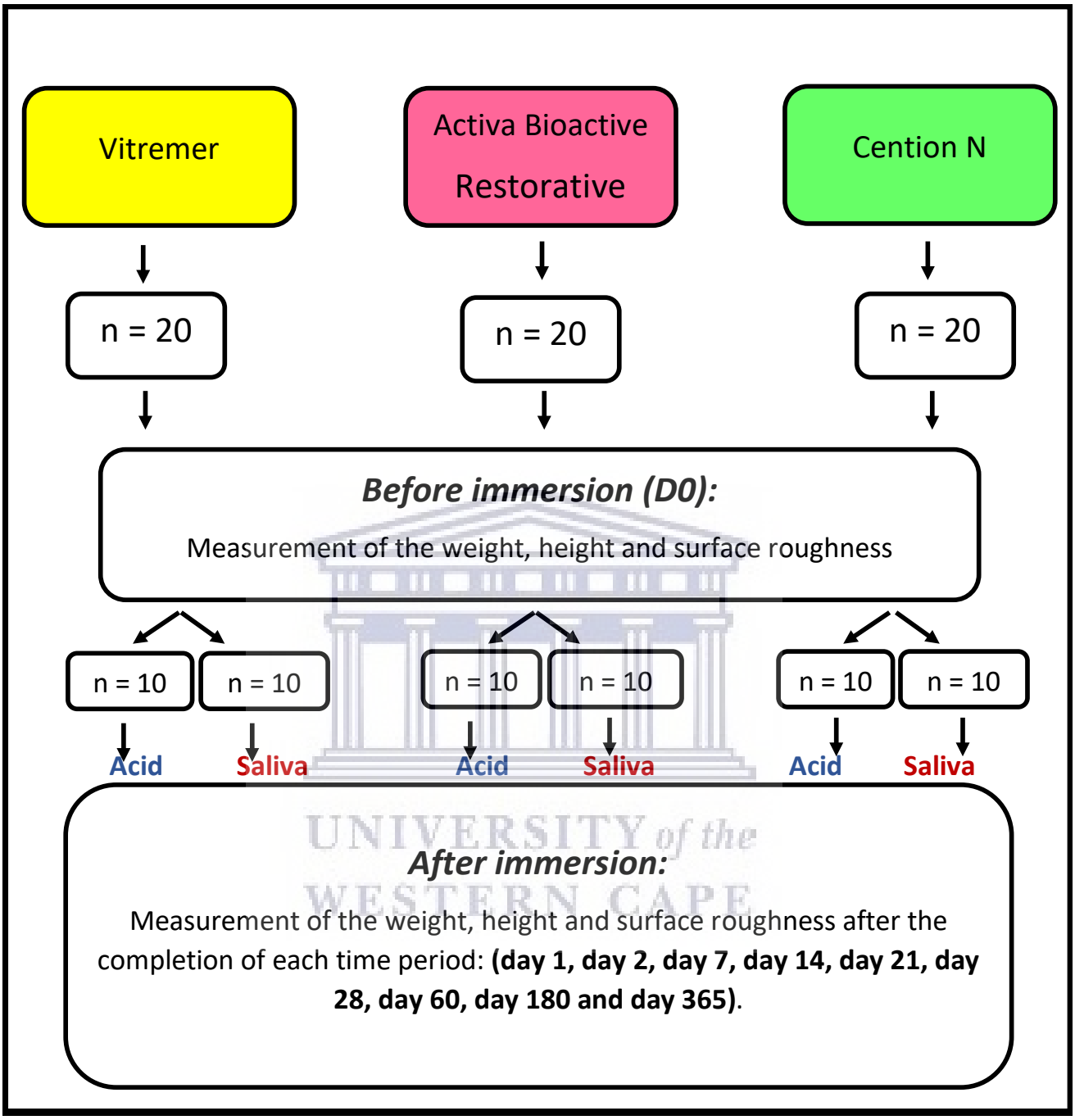


Figure (3.1): Flow chart illustrating the conceptual framework for the measurement of the height, weight and surface roughness throughout the study period.

3.6. Sampling Strategy

The sample size was determined based on previous studies (Bala *et al*., 2012). The specimens from each material were made in a standardized Teflon mould of 6 ± 0.25

mm diameter and 1 ± 0.25 mm thickness. The samples were then randomly divided through the use of block randomization and numbered as depicted in **Figure (3.1)** into two groups by a research assistant (RM), in order to blind the tester of the materials.

3.7. Ethical consideration

The protocol was submitted to the dental research (DENTREC) and biomedical research (BMREC) ethics committees of the University of the Western Cape with approval number: BM 18/9/6. This study was self-funded; the researcher did not receive any form of grant or remuneration from funding agencies or any dental materials company.

3.8. Method

3.8.1. Method for sample preparation

The restorative materials' powder and liquid ratio were meticulously weighed through the use of an electronic analytical balance (AE 240 analytical balance, Mettler, Ohio, USA) that was shown in **Figure (3.9)**. Furthermore, the materials were dispensed as per the powder/liquid ratio (PLR) of each manufacturer (Mulder, 2018). This was an essential step in the methodology, before mixing, to ensure the best mechanical properties are achieved through an accurate PLR. **Figures (3.2)** and **Figure (3.3)** illustrate the manufacturer's powder handling protocol. The manufacturer recommends mixing of Vitremer in standard powder to liquid ratio of (2.5:1) to ensure the best mechanical properties (3M ESPE, 2012). Moreover, the manufacturer advises incremental mixing through the use of cement spatula within 45 seconds until 3 minutes (3M ESPE, 2012).

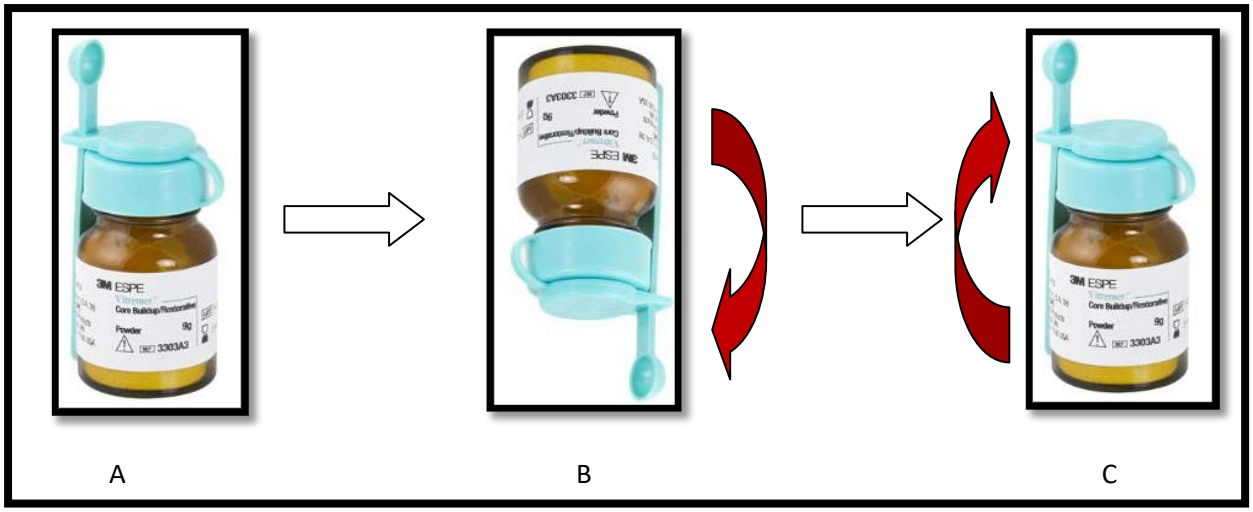


Figure (3.2): An indication of the shaking method of the Vitremer powder before weighting of the samples.

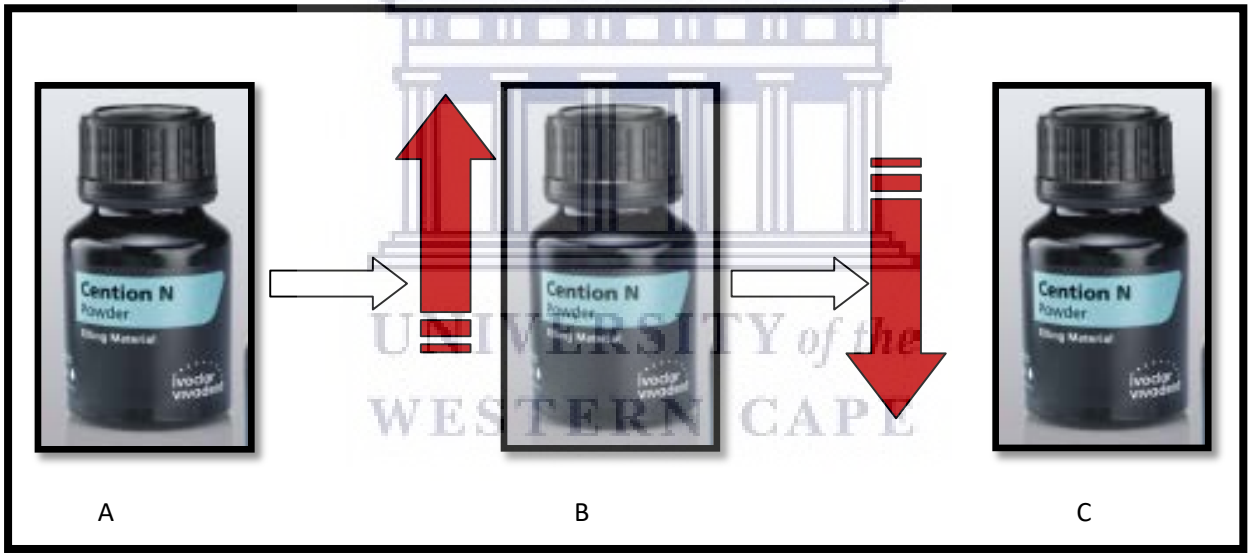


Figure (3.3): An indication of the shaking method of the Cention N powder before weighting of the samples.

This PLR ratio measure step was not completed for Activa. Activa has a syringe system where the pastes are mixed through the 20-gauge metal canula and mixing spiral. This paste-paste method ensures a calibrated mix in equal amounts of the paste to paste ratio and the expressed paste was inserted into the mold. All the materials were placed into Teflon moulds (6 mm diameter, 1 mm thickness) which had been covered on each side with a transparent polyester strip laid on a glass microscope slide to reduce the

oxygen inhibition and decrease the incidence of void formation (Palmer *et al.,* 1999). This technique has been proven in the literature to provide the smoothest surface possible for each material (Iwami, *et al.*, 1998; Pedrini *et al.*, 2003; Bala *et al*., 2012), without binding and chemical interference from the glass microscope slide. The materials were then cured through the surface of the microscope slide as depicted on the diagram below (**Figure (3.4**), using a LED light *(Elipar S10, 3M-ESPE, USA)* with an output intensity of 1200 mW/cm^2 (Elipar S10 LED curing light, 2013).

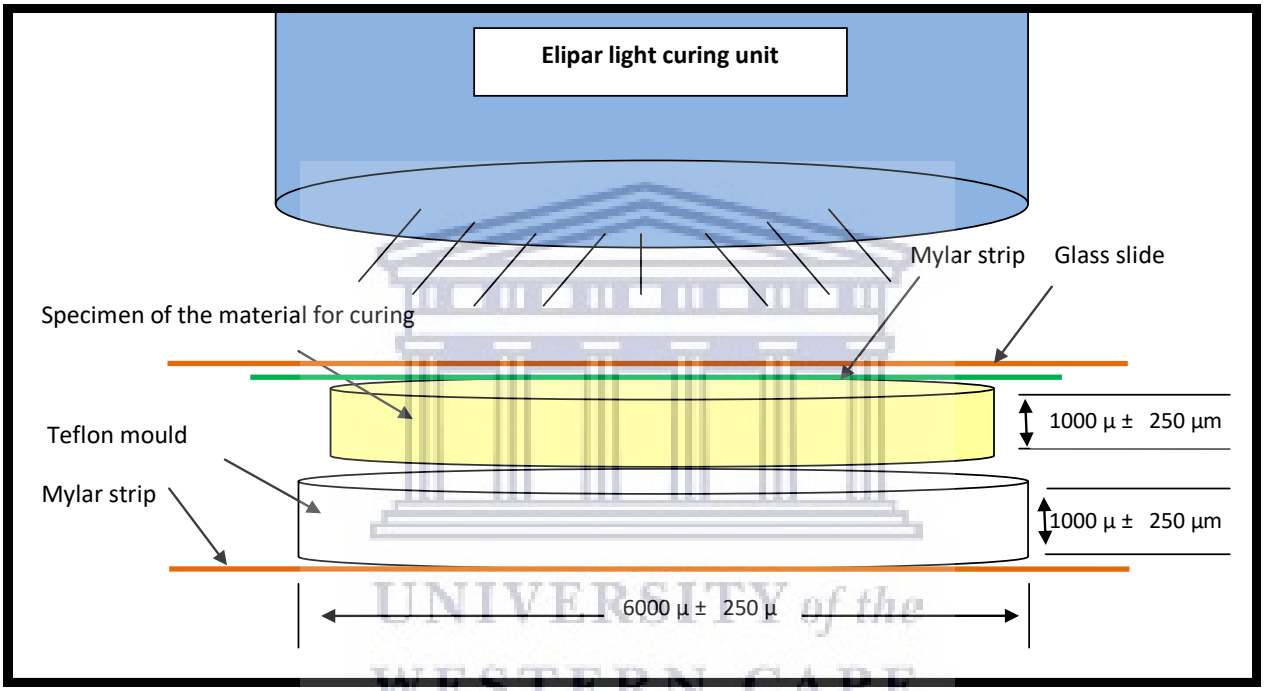


Figure (3.4): Diagram representing general specimen preparation.

Subsequently, the materials were kept at room temperature (23 ± 1 ºC) with a relative humidity of (50 ± 5%). The moulds were left on the laboratory bench for 1 hour after the light curing. For finishing, wet grit silicon carbide abrasive paper sizes 800, 1000 and 1200 *(3M, Massachusetts, USA)* were used sequentially in a circular planar motion on the materials in order to simulate the clinical finishing process. This polishing process was used based on previously published methodologies (Mulder & Anderson-Small, 2019). After finishing, each specimen was washed with de-ionized water to remove any loose particles from the material and the silica carbide paper. The specimens were then examined under the light for the presence of any obvious voids as shown in **Figure**

(3.5). All the samples were made from a single batch of materials and the preparation was done on the same occasion for each studied material. For fluoride ion release, an extra five specimens of each material were fabricated and immersed into 5 ml of de-ionized water.

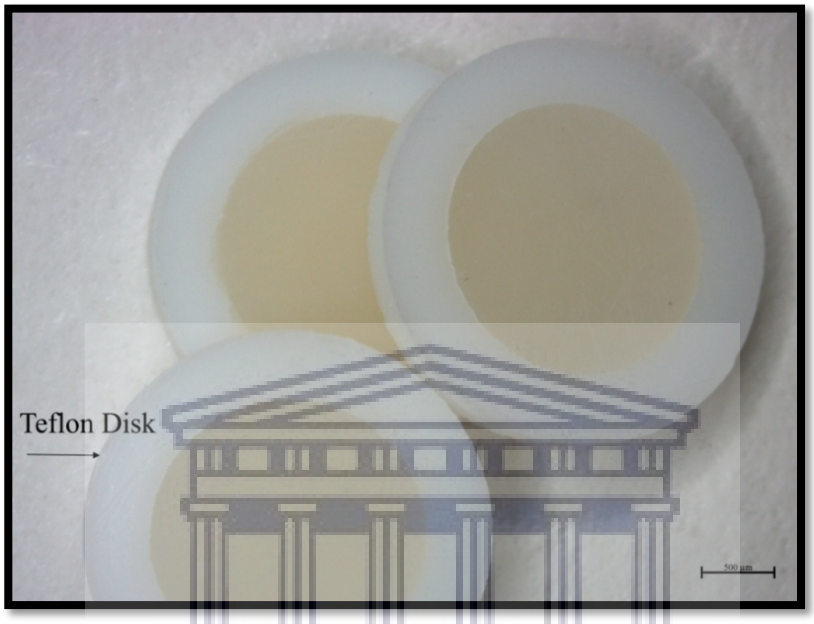


Figure (3.5): Final image for the prepared specimens before immersion.

3.8.2. Acid and saliva media

20 specimens of each material, were divided randomly into two groups and immersed to one of two media: **Group A**: acidic media (n = 10) or **Group B**: Buffered saliva (n = 10) as shown in **Figure (3.6)** below.

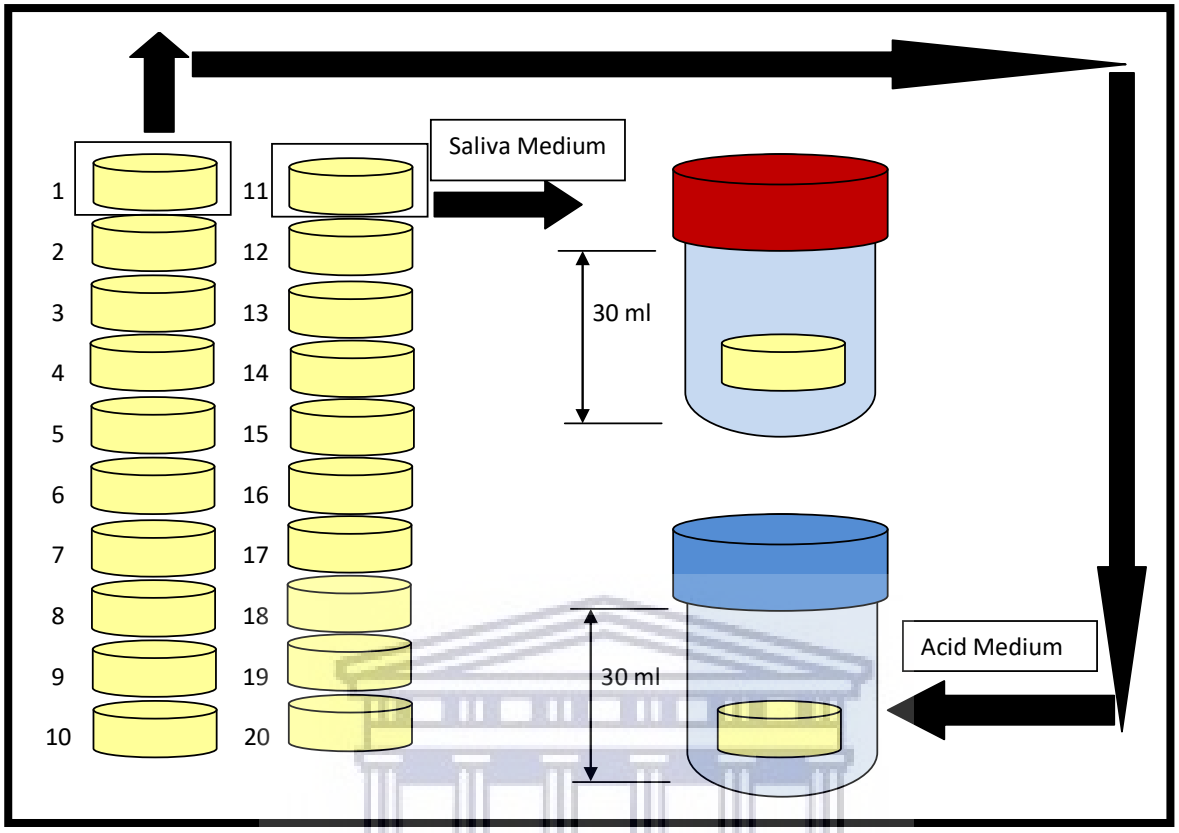


Figure (3.6): An illustration of how each material is assigned to an acid or saliva solution.

During measurements, the specimens were removed from the medium and lightly rinsed with de-ionized water and blot dried with absorbent paper before each measurement. The acidic solution was replaced after each reading over 10 different time periods from the baseline.

- **Preparation of the acidic (eroding) solution**

The acidic solution was prepared following ISO standard 9917-1; 2007 (ISO 9917-1, 2007). The acidic solution was made through mixing of 8.27 g of lactic acid and 0.92 g sodium lactate. Both of these solutions were weighed using a scale to the accuracy of 0.01 g decimal and added to 1 liter of de-ionized water. The solution was kept for at least 18 hours before use in order to allow for the hydrolysis of the lactones. The pH of the solution was adjusted through the use of hydrochloric acid (HCL) until the solution's total pH was equal to 2.74 ± 0.02. The concentration of acid was 0.1 mol/L. Litmus strip

papers were used for adjustment of the pH by means of a color indicator labeled at the back of the box.

- **Preparation of saliva (neutral) solution**

Saliva mixing was done according to the following steps:

Step 1: Tris-(Hydroxymethyl) amino-methane (TRIS) buffer preparation. TRIS is a weak base $(HOCH_2)_3CNH_2$ prepared according to the instructions on the website (https://www.aatbio.com/resources/buffer-preparations-and-recipes/). This was accompanied by calculations of the mass of the TRIS, through the molarities divided by a hundred).

Step 2: Mixing of (TRIS) buffer to the other components. TRIS was added to one liter of water. Other chemicals that were added to water include the following; calcium, phosphorus and potassium chloride (KCL), all measured to the second decimals using a scale depicted in **Figure (3.7)**. **Table (3.2)** details the composition of artificial saliva and acidic solution.

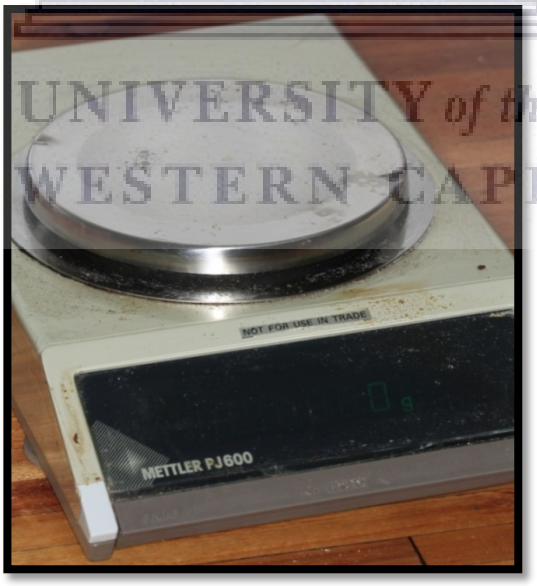


Figure (3.7): A Mettler scale used for measuring the weight of the chemicals before mixing.

Table (3.2): A detailed description of the compositions of the artificial saliva and acidic solution.

	Composition	Concentration of each component (g/L)	Description
Acidic solution	Lactic acid Sodium lactate + 1 Liter of water	8.27 g 0.92 g	Full strength HCL acid was used for adjustment
Artificial saliva	Calcium phosphorus Potassium chloride (KCL) + 1 liter of water	1.50 g 0.8833 g 111.825 g	Full strength HCL acid was used for adjustment

Step 3: Measuring of the pH

The pH values for each storage solution were determined using the litmus paper with the indicator colors. The measurements were taken before the immersion of the specimens, and repeated each time after the solution was changed.

For Artificial saliva, the pH was measured and adjusted through the use of HCL to approximately 7 and the volume of the mixture was increased to 1 liter. The artificial saliva was mixed using a stirrer (Bibby heated magnetic stirrer Hb 502, Andrew Fox Common Farm, Cheshire, UK) as shown in **Figure (3.8)** below.

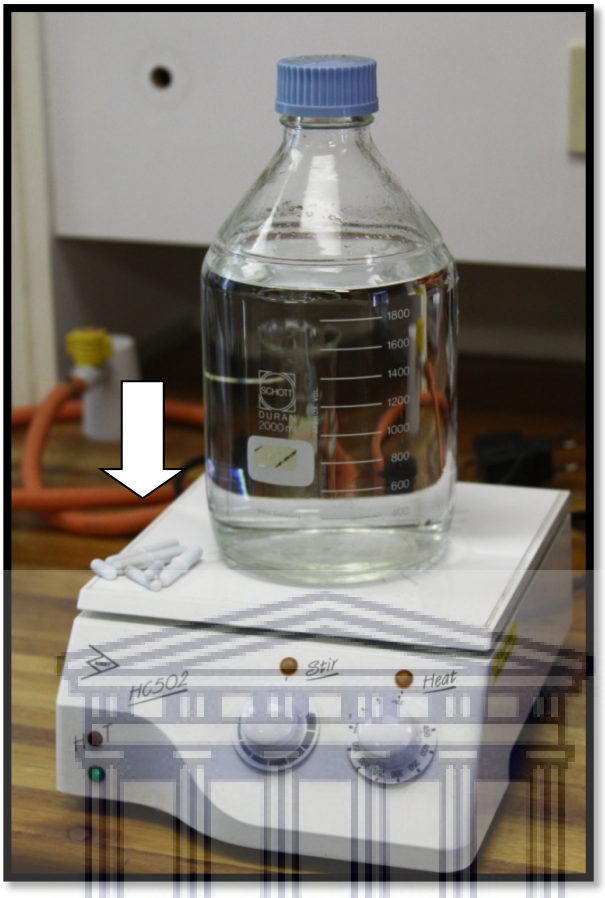


Figure (3.8): A Bibby heated magnetic stirrer Hb 502 used for mixing of the artificial saliva components. The arrow illustrates the rotating magnets that aid in the mixing process.

The principal investigator (Mohammed Jafar, R) collected the data at eleven-time intervals as follows: day 0, day 1, day 2, day 7, day 14, day 21, day 28, day 60, day 90, day 180, and day 365. Both the acid and artificial saliva solutions were replaced constantly after completion of each time interval by a new, fresh solution. Before replacement with the new solution, each bottle was rinsed with de-ionized water. The weight, height and surface roughness changes were determined on these same samples for both group A and group B. It is important to mention that the same sample was used throughout the whole experimental period. The laboratory assistant (RM) was blinded to the samples between each time interval.

3.8.3. Weight change determination

For every specimen included in the study, the weight was determined to the fourth decimal on an electronic analytical balance (AE 240 analytical balance, Mettler, Ohio, USA) that was shown in **Figure (3.9)**, to an accuracy of 0.0001 mg. The first reading (baseline reading) was taken before immersion in both media (day zero (0)); an hour after the fabrication of the specimen and light curing to ensure full maturation of the specimen. This was done according to the ISO standard 4049: 2019 (SO 4049, 2019). The specimens were not subjected to any form of desiccation that could result in the removal of the bound water which is considered essential for the maturation of the cements (Kanchanavasita *et al.*, 1997). After the specimens had been immersed in the acid and saliva medium for 24 hours, they were removed, blot dried and weighed immediately. Upon completion of the measurement, the specimens were kept moist in tissue paper and were immediately re-immersed in the media bottles after they were changed. This method of measurement was repeated as follows: day 1, day 2, day 7, day 14, day 21, day 28, day 60, day 90, day 180 and day 365.

Figure (3.9): Mettler chemical scale used for weight measurements.

3.8.4. Height change determination (thickness change)

For height determination, the micrometer screw gauge, which measures up to 0.0000 µm decimal was used to measure the height of the specimens. Samples had been inserted into the area labeled in **Figure (3.10)** below and the reading was recorded from the center of the specimens.

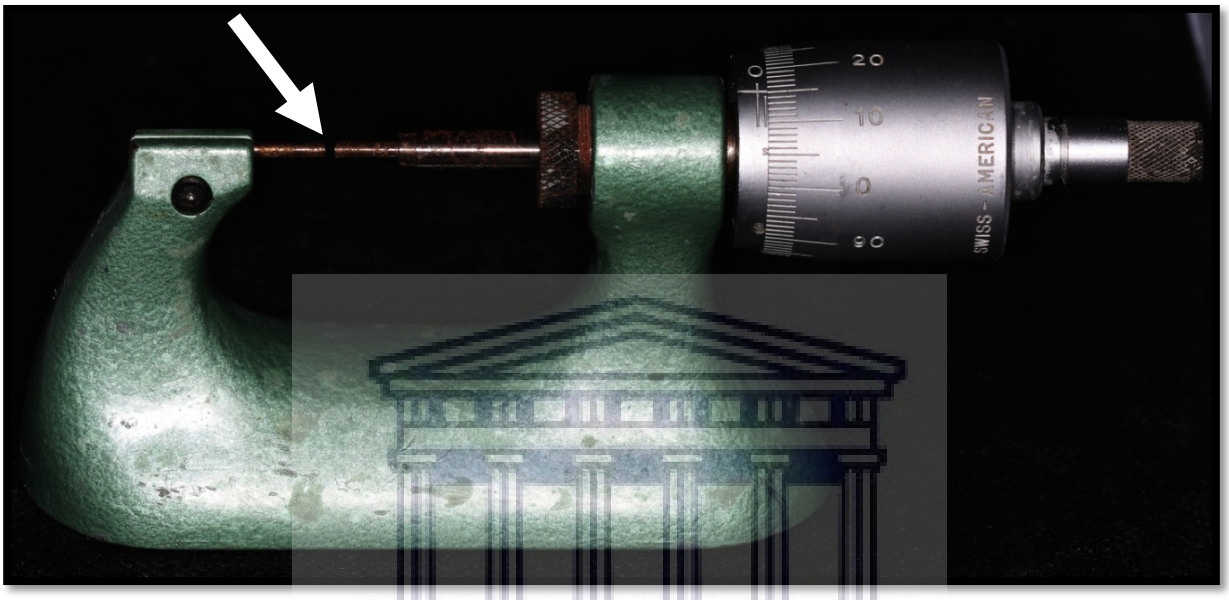


Figure (3.10): The micrometer screw gauge for the height measurements. The arrow shows the area where the material is attached during measurement of the height (in between the two arms).

The height measurements were taken at day 0 (before immersion) from each sample of the studied materials, and then after immersion in both media after the following time periods: day 1, day 2, day 7, day 14, day 21, day 28, day 60, day 90, day 180 and day 365.

3.8.5. Baseline surface roughness measurements

Surface roughness (Ra) was measured through the application of parallel measurements at standardized positions using the Model Leeb 423 *(Chongqing Leeb Instrument co Ltd, China)* as shown in **Figures (3.11) and (3.12)**. The standard sensor had a measuring range of 0.005 - 16 µm Ra. The component of the machine was illustrated in **Figure (3.12).**

Figure (3.11): The surface roughness tester assembly from the outside (the standard configuration).

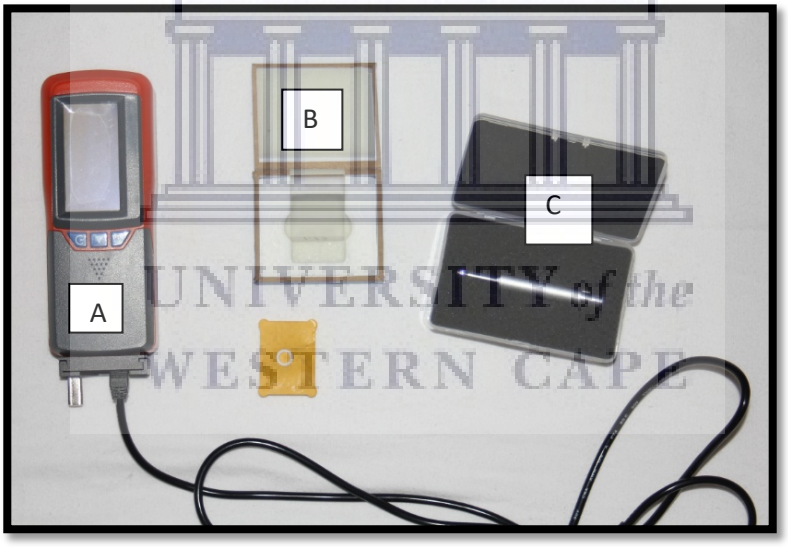


Figure (3.12): The components of the machine: A) Main Unit attached to the power adapter. B) Model for multi-standard groove. C) Standard sensor.

Figure (3.13): Surface roughness machine (Leeb 432 Digital Portable Surface Profile Gauge Precision Roughness Meter with RA RZ range 13 parameters).

The testing parameters used in the study were surface roughness (Ra), Filter set at Gauss, the assessment length (λc) at 0.8 mm x n5 (assessment length (Ln = lr x n); Ln = 3.2 mm) (ISO 4288, 1998) and the range at ± 80 µm. The standard stylus with a natural diamond 90º cone angle and a 5 µm tip radius was used. The stylus applied a force to the sample of < 4 mN. The travelling speed (Vt) for the above parameters was 0.135 mm/s and the measurement accuracy ± 10%.

Prior to commencing the surface roughness measurements at different time intervals, the specimens were washed with de-ionized water to prevent any effect of the acid or saliva on the Ra sensor. Calibration of the device was completed before Ra data collection commenced on the Ra reference block provided with the Ra meter. The calibration was repeated after measuring every five specimens.

Baseline measurements were taken at the beginning of the experiment before the immersion of the three materials (at day 0). After that, the measurement was repeated at several points of time up to the period of one year after immersion. Throughout this period, each specimen from the total of 60 specimens was measured on both sides as illustrated in **Figure (3.14)**. The pattern of measuring the surface roughness is through following two parallel lines on the surface of each circular shaped specimen. After that,

the specimens were rotated 90 degrees on the same plane in order to measure the perpendicular two parallel lines. This method of measurements was followed for all the specimens and performed by one investigator (Mohammed Jafar, R) to ensure the reliability of the data. Each specimen was flipped upside down and the reverse plane measured using the same method to include a further four measurements. In the end, an average of eight measurements was used to calculate the mean Ra of each specimen. **Figure (3.14)** shows the lines for measuring the surface roughness in each specimen.

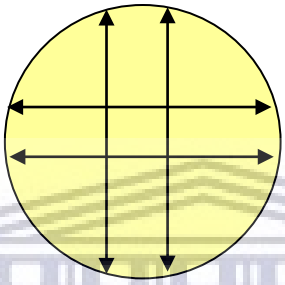


Figure (3.14): Illustration of the four lines used to measure the surface roughness on both upper and lower occlusal surfaces on each specimen.

3.8.6. Determination of the release of fluoride into the de-ionized water

Five specimens were prepared from each material according to the manufacturer's instructions and then placed into cylindrical Teflon moulds (6 mm diameter × 1 mm height). The materials were pressed between two Mylar strips-covered glass slides (Yip *et al.*, 1999). Thereafter the three materials were cured through use of a LED light-cure unit *(Elipar S10; 3M-ESPE, USA).* The light-cure was applied to both sides of the moulds following the manufacturer's instructions for each material for up to 40 seconds. After that, the three materials were allowed to stand for complete setting on the laboratory bench for one hour. After the material had set, dental floss was ligated to each specimen through the use of a white wax (name the wax). Each specimen for each material was allowed to hang in 5 ml in a container of de-ionized water. A total of 15 containers were stored at room temperature (23 ± 2°C), with a relative humidity of 50 ± 5% (Mulder & Anderson-Small, 2019; Mulder *et al*., 2019). The solutions were

replaced upon completion of the following time periods: day 1, day 2, day 7, day 14, day 21, day 28.

- ***TISAB (Total ionic strength adjustment buffer) preparation***

The TISAB II and III were made in accordance with the recommendation by Orion research (Orion Research Incorporated, 2016). 500 mL of distilled water was placed in a 1-litre volumetric flask. In a fume cupboard, 84 mL of concentrated HCL (36-38%) was added to the distilled water. The volumetric flask was placed on a magnetic stirrer on maximum speed. 242 g of TRIS (hydroxymethyl) amino-methane was added to this mixture. The last powder added was 230 g of Sodium Tartrate ($Na_2C_4H_4O_6 – 2H_2O$). Once the medium reached room temperature, additional distilled water was added to the 1-litre volumetric mark.

- ***pH determination***

The pH of the resultant diluent was assessed with an Ohaus pH meter (Ohaus Corporation, model Starter 3100, USA) that was shown in **Figure (3.15)** after it was calibrated with pH 4 and pH 7 standards.

Figure (3.15): The fluoride device with technical specification.

3.8.7. Examination of the specimens under the scanning electron microscope (SEM)

Of the 60 specimens used for the quantitative part, a total of 6 samples were chosen using simple randomization to investigate the studied materials qualitatively: two samples for each material; one sample represents the specimen that was immersed in acid media (I) and the other in artificial saliva (II). The rings were not removed from those specimens in order to take the stereo-microscopic and SEM images pre-experimentally and post- experimentally. Images were taken In order to determine changes in the surface roughness at the microscopic level. The original samples were placed onto double sided carbon tape, which in turn were placed onto an aluminum SEM stub. No coating was done on the samples as the samples were analyzed using a low vacuum SEM microscope.

The samples were loaded into a Thermo Fisher Phenom ProX SEM (Thermo Fisher, Phenom, Eindhoven, Netherlands). A 4-quadrant Phenom Backscattered Electron (BSE) Detector and Phenom ProSuite SEM software were used to generate images. For Backscattered Electron detection (BSD), operating conditions of 10 kV accelerating voltage and a spot size of 3.3 mm with a working distance of 7-9 mm were applied. Images were captured in random areas and at a range of magnifications, to characterize sample morphology. This facilitates comparison of sample images. No coating was used to allow low vacuum SEM-EDS for the instrument used in this section of the methodology. Furthermore, better resolution of the photos could be achieved without the use of the coating.

Images were taken at magnifications of 750X, 1000X and 1500X **as shown in Appendix C**. These three magnifications ensured proper visualization of the surface. Each instrument's magnification was different as it had to be done through the use of different screen monitors and pixels. Yet, valid comparison can be made with such a variation.

3.9. Statistical analysis

Statistical analysis was completed using IBM SPSS version 26 for Microsoft operating systems (significance level of 5%) (Bala *et al*., 2012; Nagi *et al.*, 2018). Normality tests were first applied to the data using Kolmogorov-Smirnov and Shapiro-Wilk tests. For measurement of the association between the weight, height and surface roughness, a simple linear regression test was applied.

3.10. Validity and reliability

To ensure the validity and reliability of the results, the samples were examined and tested by one examiner (Mohammed Jafar, R). The three materials were placed in a Teflon Mould which had constant dimensions. For the hand mixed materials (Vitremer and Cention N, the materials were weighed before mixing to get the optimum and uniform ratio of dispersion. Furthermore, the method of mixing was performed according to the manufacturer's instructions. In addition, one light-cure device was used for curing all the specimens (*Elipar S10 Curing Light, 3M, USA)*. A light intensity of 1200 mW/cm^2 was uniformly used to ensure equal output of the light to the three materials. It is also important to mention that the intensity of the light is not affected by the battery level as stated above.

CHAPTER IV: RESULTS

The results of the present study are divided into two components: *the quantitative part* which was analyzed through the use of the SPSS version 26 and *the qualitative part* that was demonstrated through the use of scanning electron microscopy.

4.1. Normality test

Prior to the application of any statistical analysis to the raw data, normality tests were performed through the use of the Kolmogorov–Smirnov test and the Shapiro-Wilk test. The results of the normality test showed that the data was skewed and not normally distributed ($p < 0.05$). Furthermore, the Q-Q plot of the data showed a deviation from the line, confirming that the data was indeed skewed. Therefore, the data was analyzed through the use of non-parametric tests; a simple linear regression analysis for the association and a Kruskal-Wallis analysis for comparison. In order to clarify the results, the following **Figure (4.1)** shows the keys for the colors, and abbreviations.

Table (4.1): Keys for colors and abbreviations in this chapter.

Abbreviation, symbol or color	Description
V	Vitremer
A	Activa
C	Cention N
≥	Insignificantly higher
>	Significantly higher
Dark Blue line	Linear association in acidic media
Red line	Linear association in saliva media
in the background (yellow)	Vitremer

in the background (pink)	Activa
in the background (green)	Cention N
in the background (light blue)	Acidic media
in the background (brown)	Saliva media

4.2. Association of the studied variables within each material in different media

4.2.1. Weight changes

In order to answer the first specific objective of the present study, which was to determine the association between the weight and time interval for the three studied materials, we ran a simple linear regression. In acidic media, out of the three materials, only Vitremer showed a significant weight loss (p = 0.007) in acidic media compared to the control material. Both Activa and Cention N showed no significant difference in weight change after one-year immersion in acidic media, (p = 0.862) and (p = 0.957) respectively. The following graphs show the association of the change in weight in relation to the studied materials; Vitremer, Activa and Cention N respectively, from the baseline (day 0) to one year. In the *artificial saliva media*, there was an observed weight gain in Vitremer and Activa materials. However, this weight gain was not statistically significant for both materials; Vitremer p-value was (p = 0.503) and Activa was (p = 0.830). On the other hand, Cention N showed a reduction in weight, however, this reduction was not statistically significant either (p = 0.948).

4.2.1.1. Weight change of Vitremer over a period of one year

The following graphs show the association between the weight of Vitremer in acid media and saliva media respectively over a one year period. Following the same pattern, Activa and Cention N were presented. Every group of vertical dots represents

one point of time in which the measurement was taken. Each dot represents one specimen.

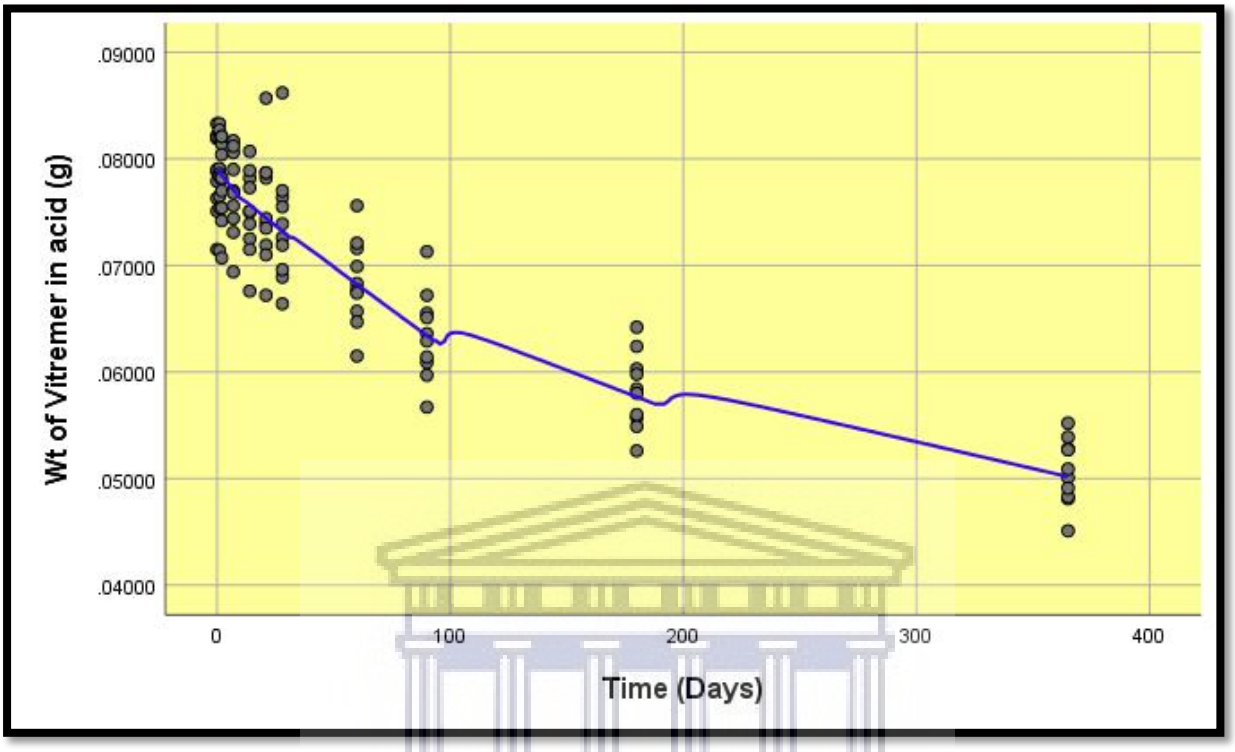


Figure (4.1): Weight of Vitremer in acidic media over 10 periods of time after the baseline values. There was a significant negative association (p = 0.000) between the weight of the Vitremer and its immersion in acidic media over a one year period (-8.022E^{-5}). For every change in unit time, the slope was negative by (-8.022E^{-5}).

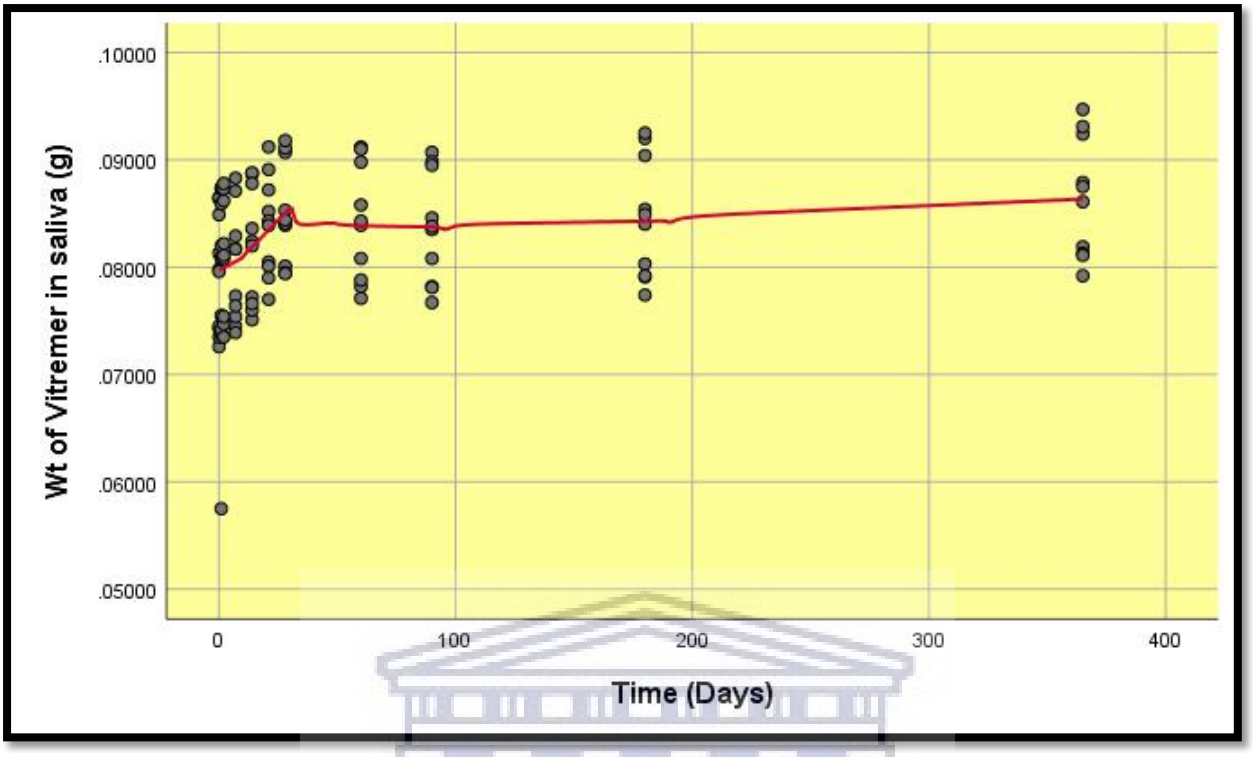


Figure (4.2): Weight of Vitremer in saliva media over 10 periods of time after the baseline values. There was a significant positive association (p = 0.002) between weight of Vitremer and its immersion in saliva media over a one year period. For every change in unit time, the slope was positive by ($1.665E^{-5}$).

4.2.1.2. Weight change of Activa bioactive restorative over the period of one year

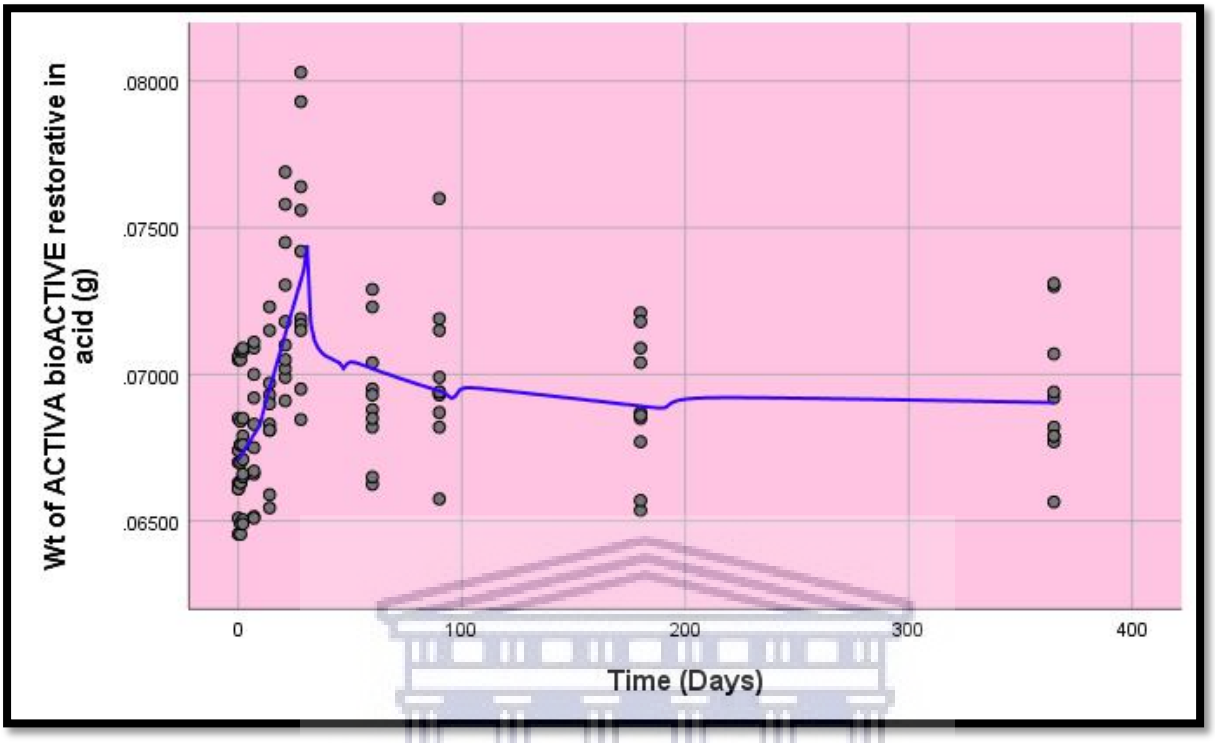


Figure (4.3): Weight of Activa in acid media over 10 periods of time after the baseline values. There was a non-significant positive association (p = 0.698) between the weight of the Activa and its immersion in acidic media over a year period. For every change in unit time, the slope was positive by ($1.083E^{-6}$).

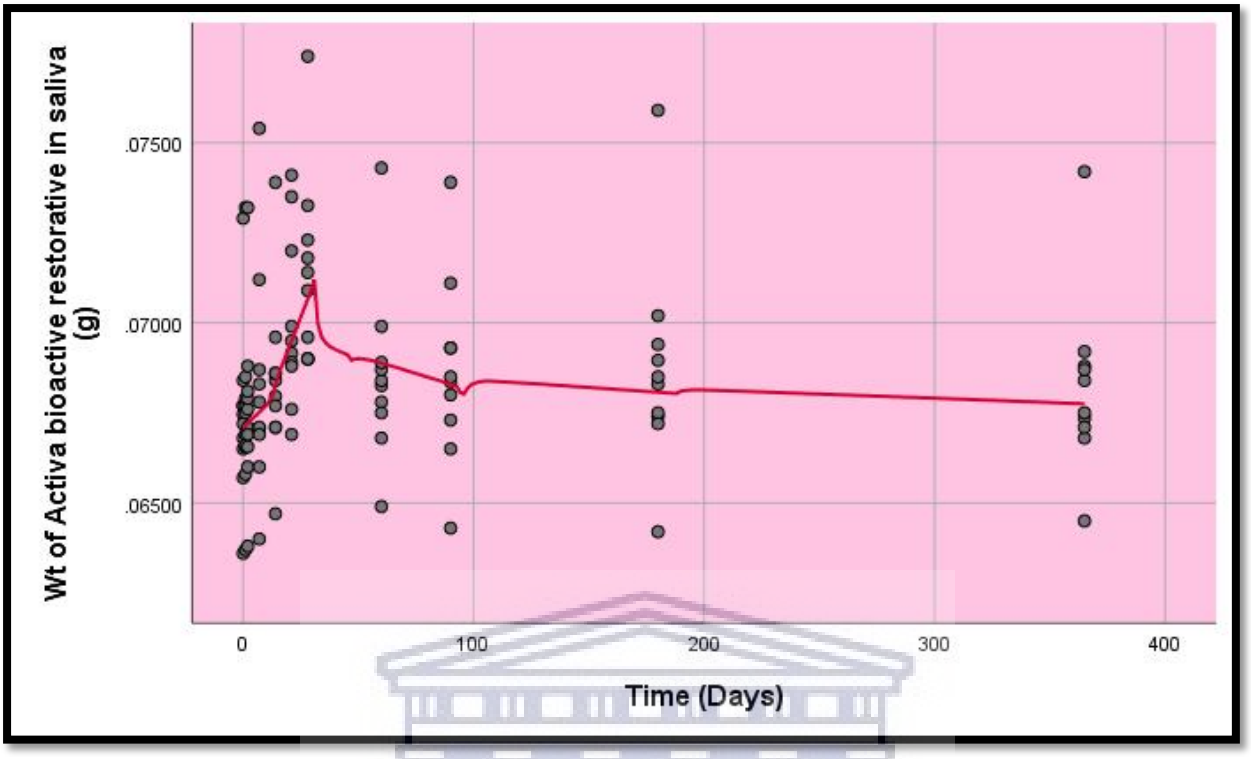


Figure (4.4): Weight of Activa in saliva media over 10 periods of time after the baseline values. There was a non-significant negative association (p = 0.998) between the weight of the Activa and its immersion in saliva media over a one year period. For every change in unit time, the slope was negative by ($-7.2841E^{-9}$).

4.2.1.3. Weight change of Cention N restorative over a period of one year

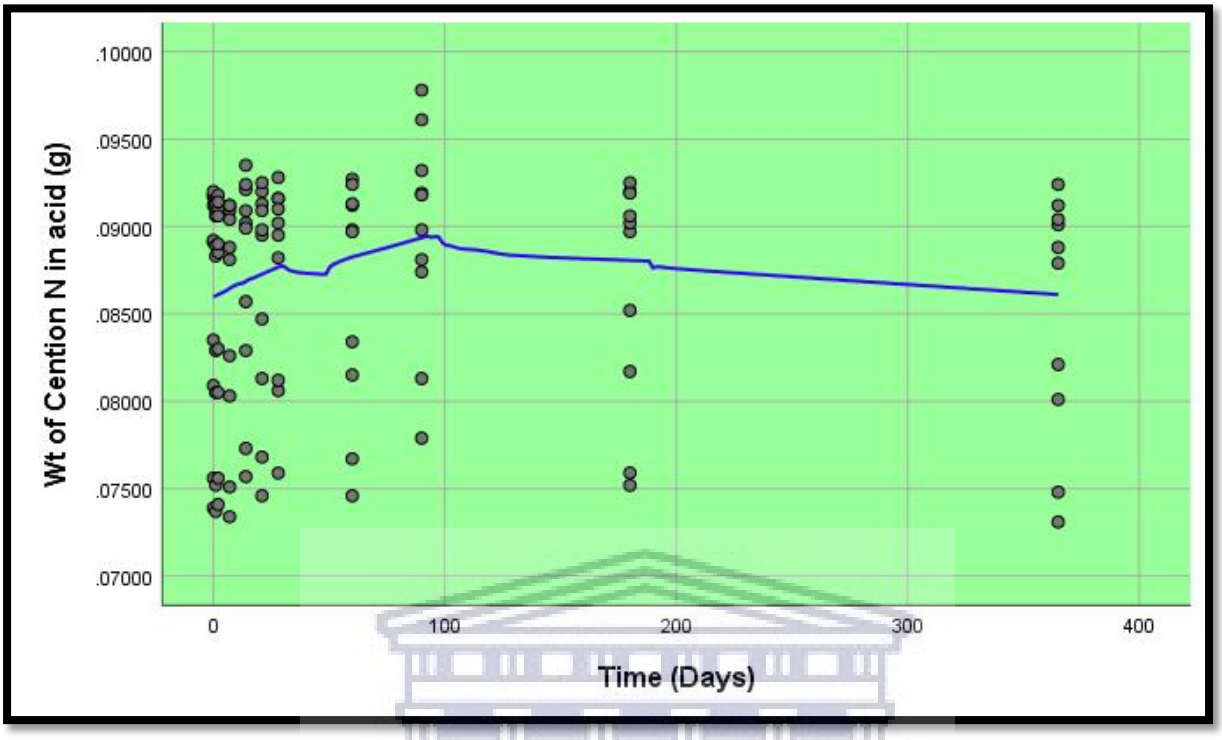


Figure (4.5): Weight of Cention N in acid media over 10 periods of time after the baseline values. There was a non-significant negative association (p = 0.843) between the weight of the Cention N and its immersion time in acidic media over a one year period. For every change in unit time, the slope was negative by ($-1.150E^{-6}$).

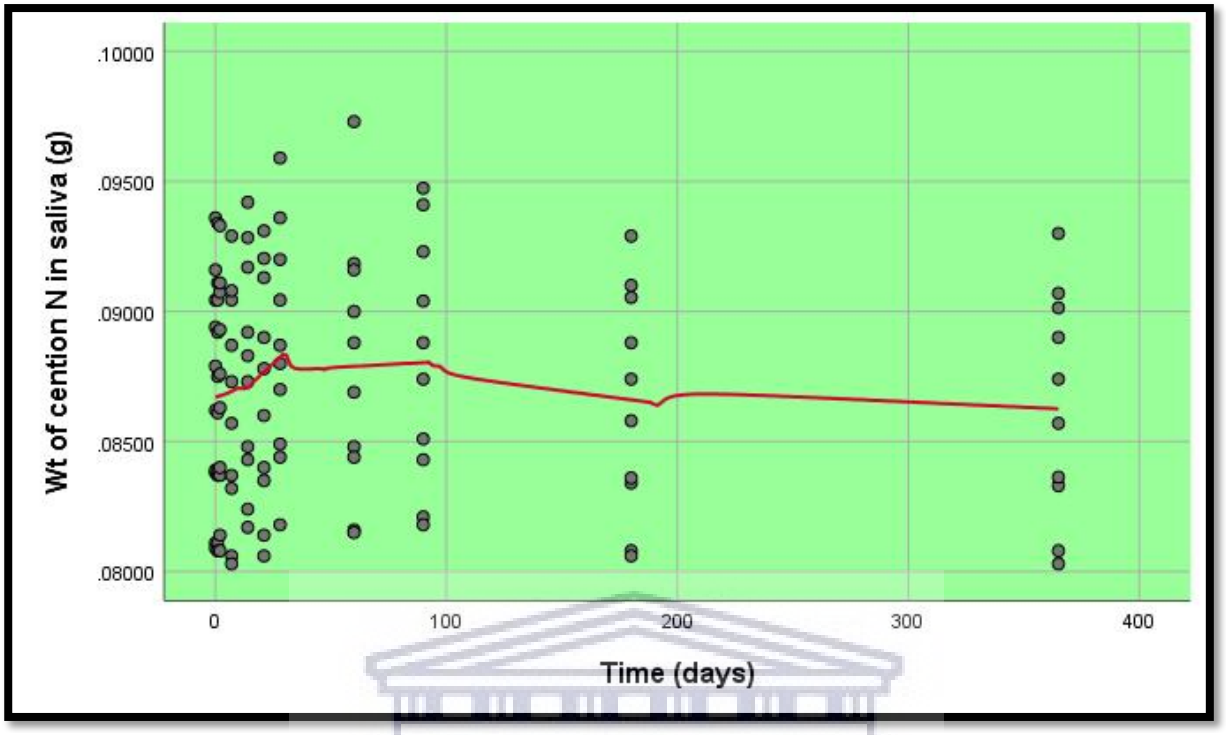


Figure (4.6): Weight of Cention N in saliva media over 10 periods of time after the baseline values. There was a non-significant negative association *(p* = 0.617) between the weight of the Cention N and its immersion time in saliva media over a one year period. For every change in unit time, the slope was negative by ($-1.946E^{-6}$).

4.2.2. Height changes

As done for weight, the association between the height and time interval for the three studied materials was determined for one year through the use of simple linear regression. *In acidic media,* all the specimens from the three materials showed a gradual decrease in height. However, only Vitremer showed a statistically significant height loss (p = 0.007) in comparison to Activa (p = 0.971) and Cention N (p = 0.626). Thus, the results followed the same pattern as the weight loss in acidic media as discussed in the section above. The following graphs depict the changes in height for the studied materials; Vitremer **Figures (4.7) and (4.8)**, Activa **Figures (4.9) and (4.10)**, and Cention N **Figures (4.11) and (4.12)**, respectively from the baseline (day 0) for a period of one year.

With immersion in *artificial saliva media*, there was an observed height gain in Vitremer and Activa material. However, this height gain was not statistically significant for both materials; for Vitremer the p-value was (p = 0.177) and for Activa (p = 0.928). Cention N on the other hand, showed some reduction in height, even though this reduction was not statistically significant as well (p = 0.621).

4.2.2.1. Height change of Vitremer over a period of one year

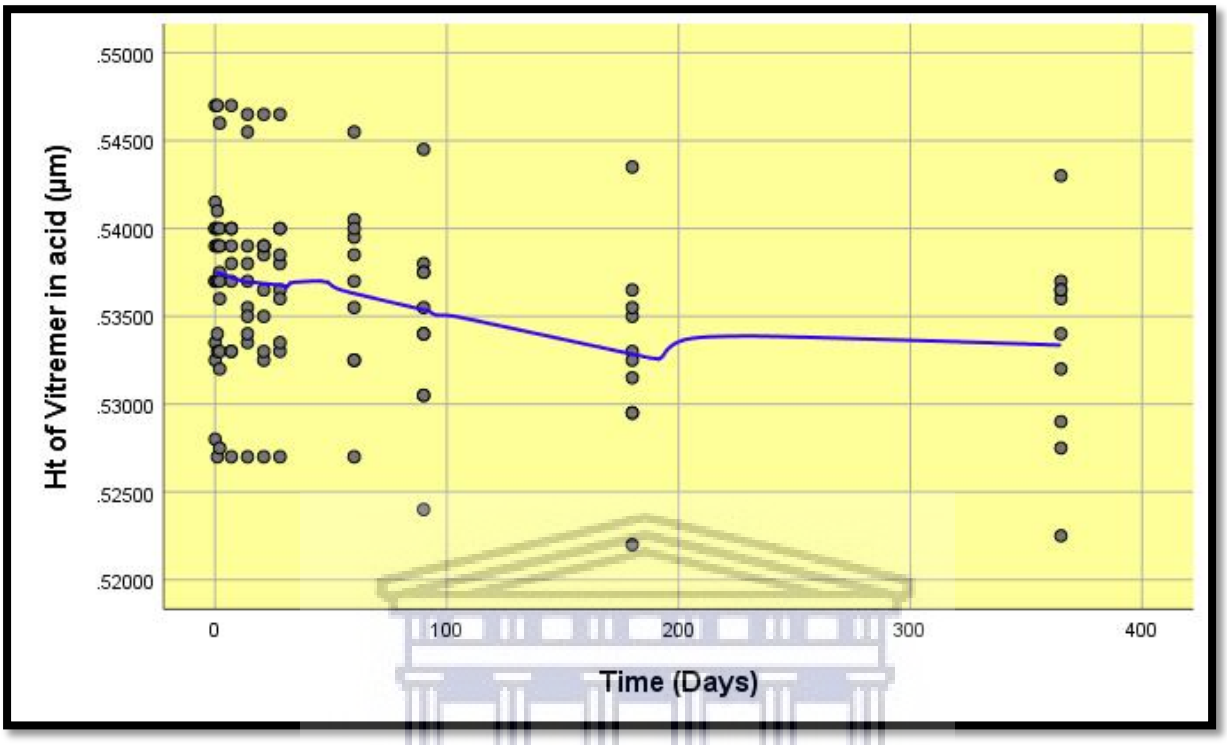


Figure (4.7): Height of Vitremer in acidic media over 10 periods of time after the baseline values. There was a statistically significant negative association *(p* = 0.007) between the height of the Vitremer and its immersion time in acidic media over a year period (-1.294E^{-5}). For every change in unit time, the slope was negative by (-1.294E^{-5}).

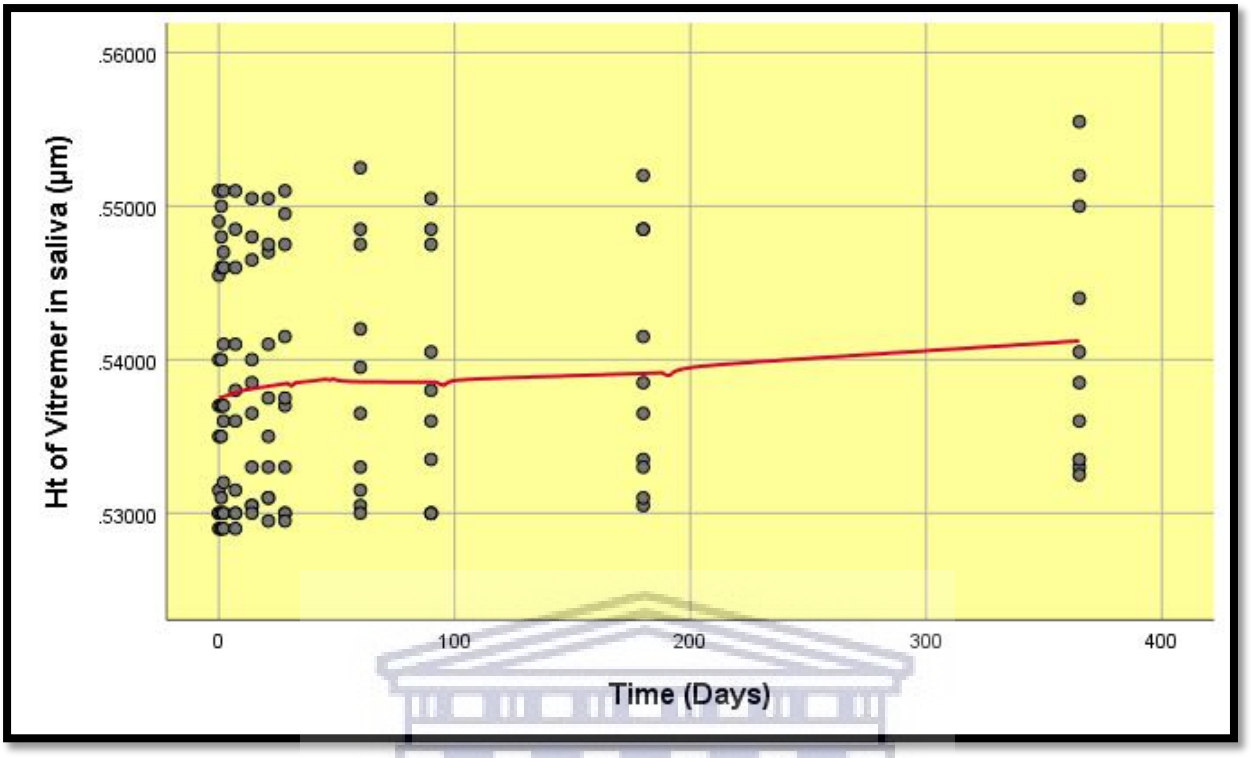


Figure (4.8): Height of Vitremer in saliva media over 10 periods of time after the baseline values. There was a positive association (p = 0.177) between the height of the Vitremer and immersion time in saliva media over a one year period ($9.42E^{-6}$). For every change in unit time, the slope was positive by ($9.42E^{-6}$).

4.2.2.2. Height change of Activa bioactive restorative over a period of one year

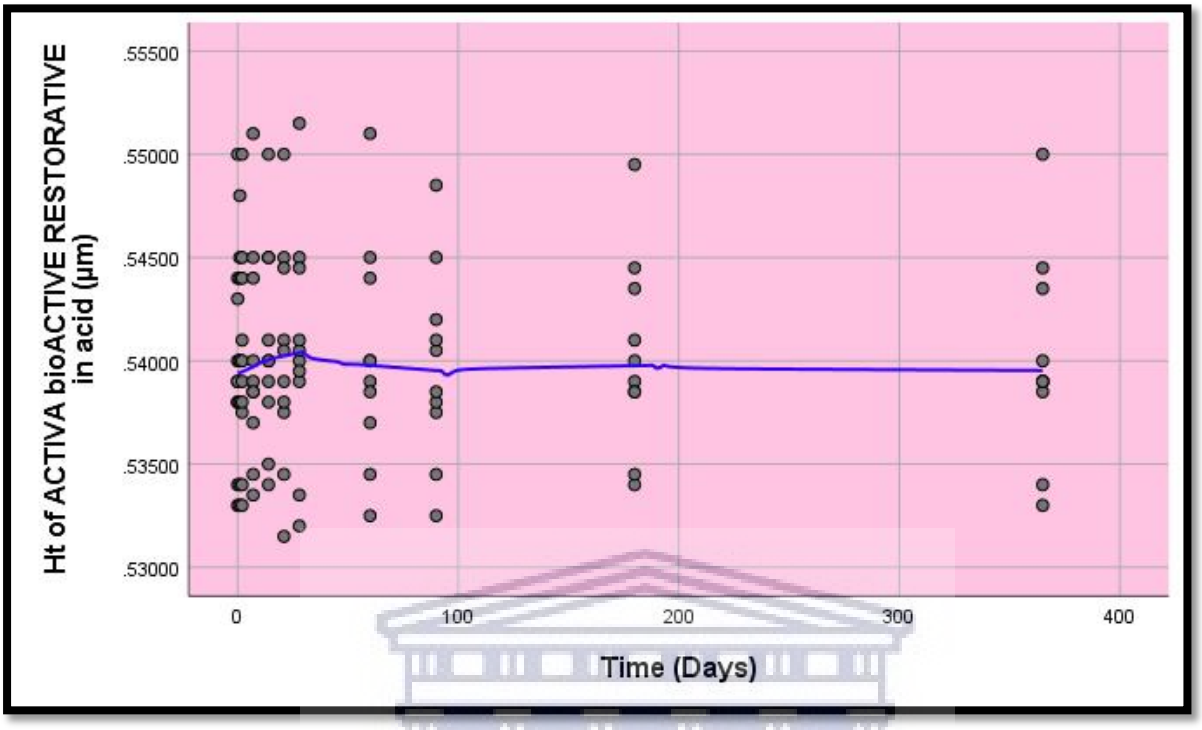


Figure (4.9): Height of Activa in acid media over 10 periods of time after the baseline values. There was a negative association (p = 0.971) between the height of the Activa and its immersion in acidic media over the period of one year ($-1.598E^{-7}$). For every change in unit time, the slope was negative by ($-1.598E^{-7}$).

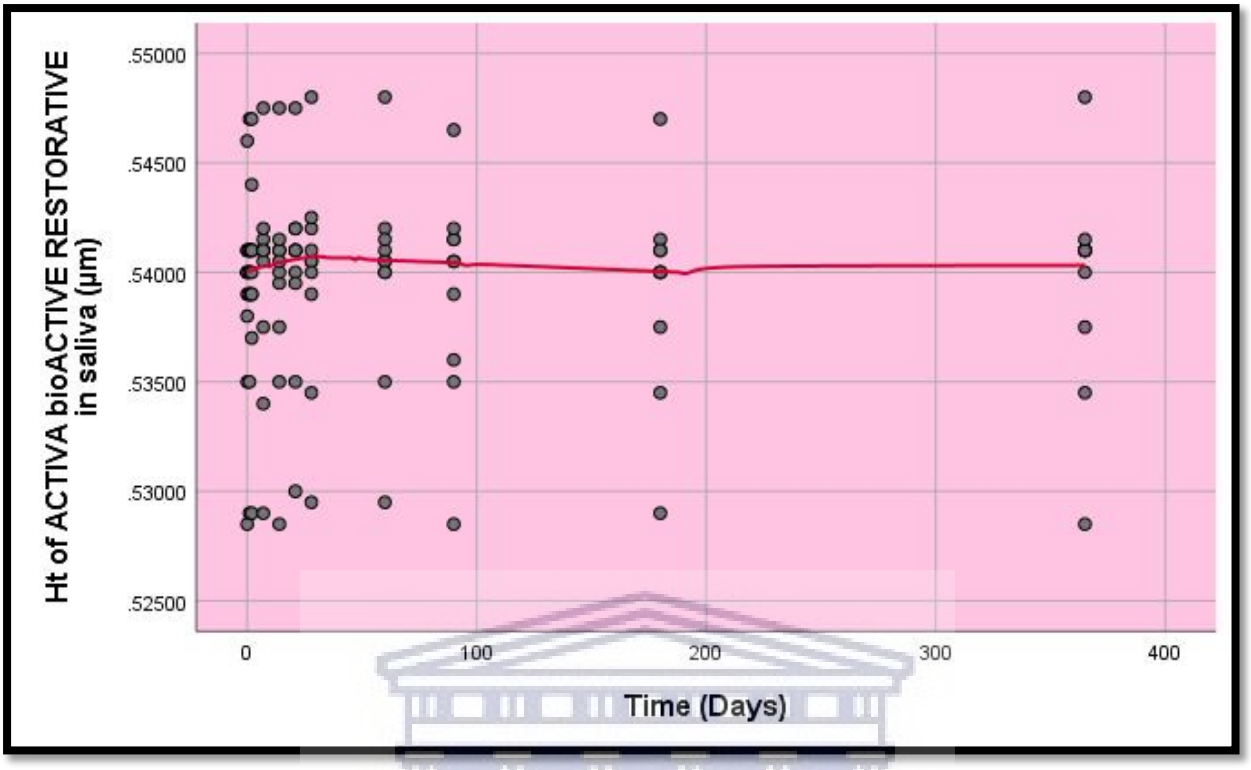


Figure (4.10): Height of Activa in saliva media over 10 periods of time after the baseline values. There was a negative association (p = 0.928) between the height of Activa material and its immersion in acidic media over a one year period ($-3.727E^{-7}$).

4.2.2.3. Height change of Cention N over a period of one year

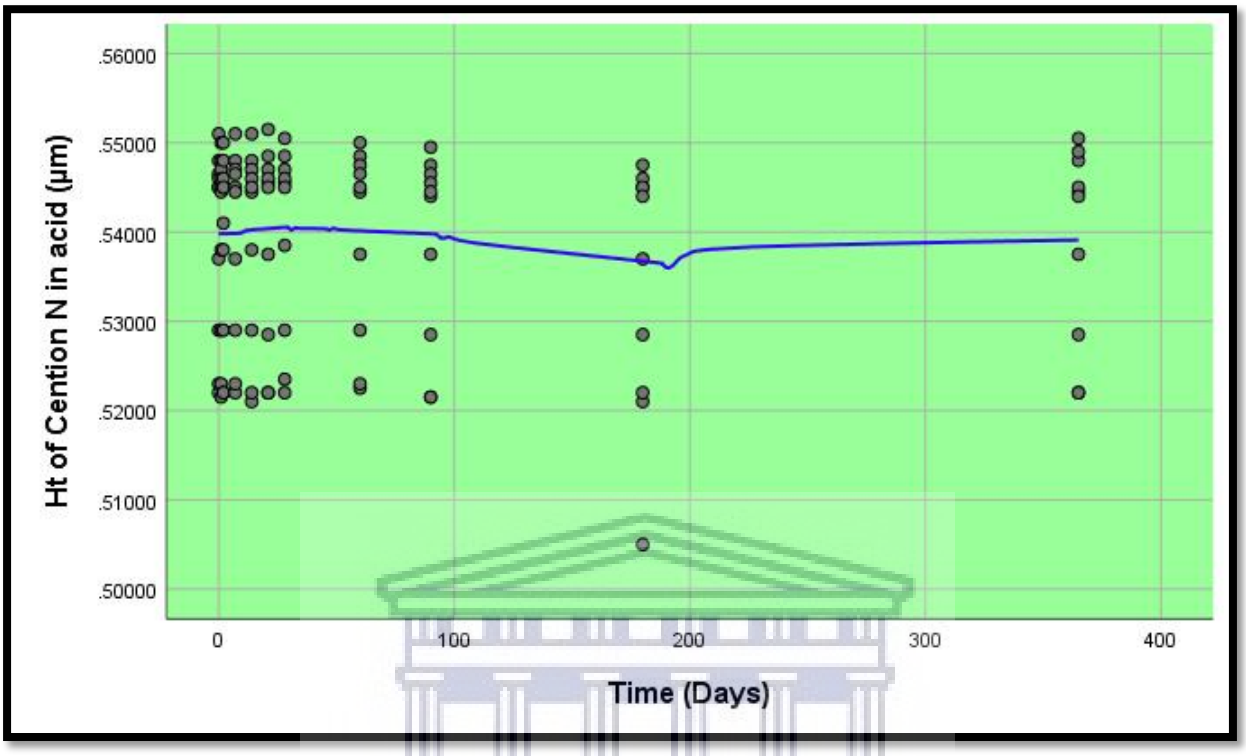


Figure (4.11): Height of Cention N in acid media over 10 periods of time after the baseline values. There was a non-significant negative association *(p* = 0.626) between the height of Cention N and its immersion in acid media over a period of one year (-4.735E^{-6}).

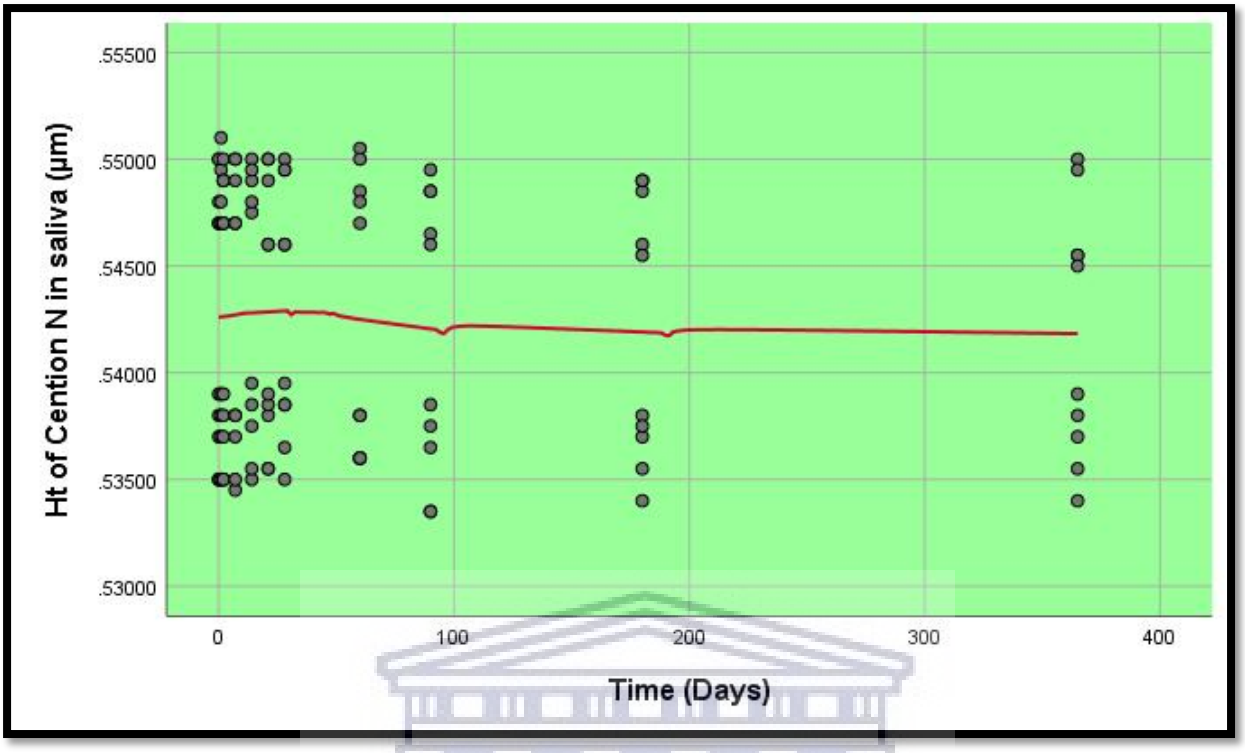


Figure (4.12): Height of Cention N in saliva media over 10 periods of time after the baseline values. There was a non-significant negative association (p = 0.621) between the height of Cention N and its immersion in acid media over a period of one year (-2.655E^{-6}).

4.2.3. Surface roughness changes

The results of a simple linear regression show a statistically significant positive association between the Ra of Vitremer and the duration of its immersion in acidic media (p = 0000), Cention N showed the same significant association after a year as well (p = 0000). Nevertheless, the association between the surface roughness of Activa restorative material and its immersion in acidic media for one year was not statistically significant (p = 0.633).

For saliva media immersion, a positive association was observed in the surface roughness of the three study materials. This association was however not statistically significant for the three materials; the p-value of Vitremer was (p = 0.676), Activa (p = 0.201) and for Cention N (p = 0.154).

4.2.3.1. Changes in Ra values of Vitremer over a period of one year

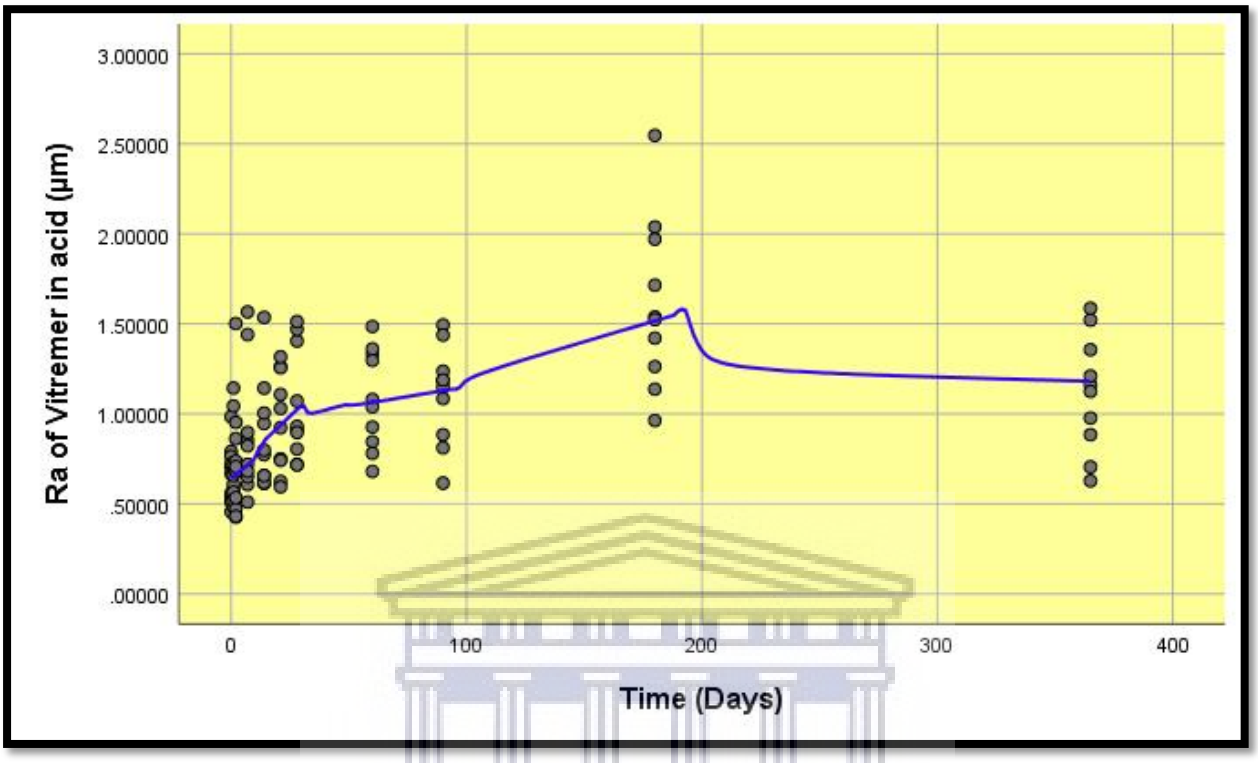


Figure (4.13): The surface roughness (Ra) of Vitremer in acidic media over 10 periods of time after the baseline values. There was a significant positive association (p = 0.001) between the Ra of Vitremer and immersion in acidic media over a one year period. For every change in unit time, the slope was positive by (p = 0.001).

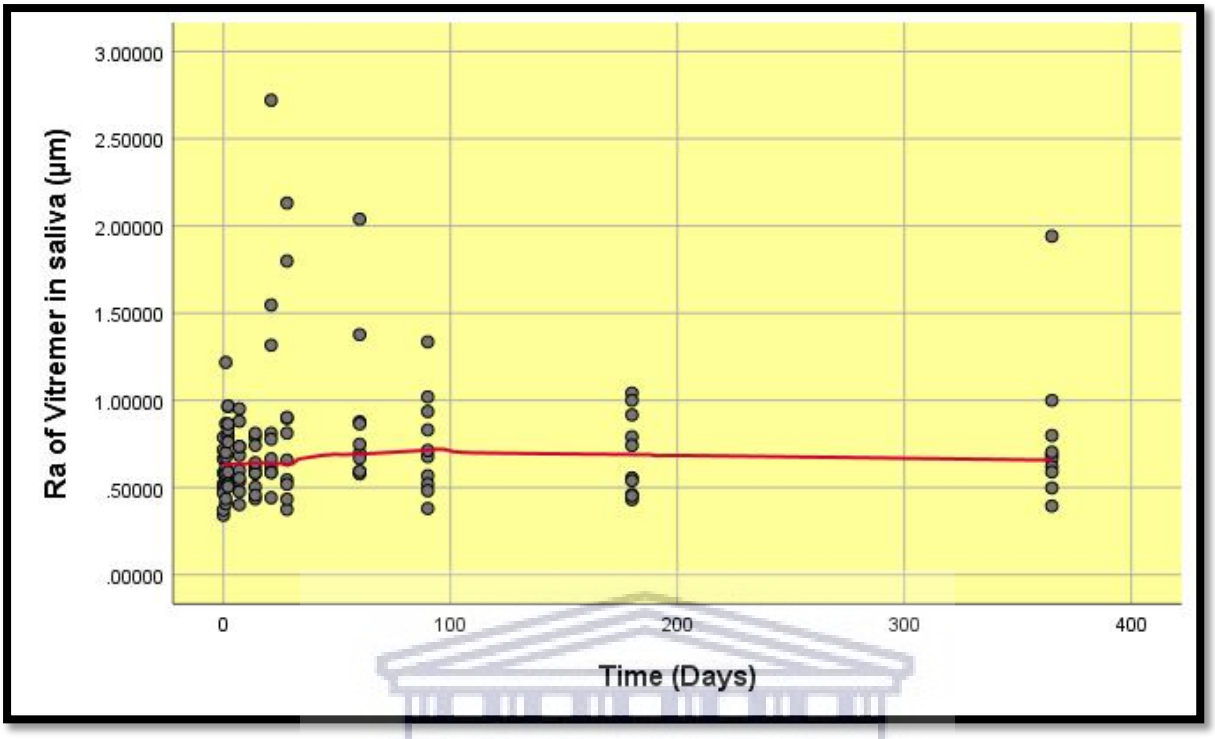


Figure (4.14): The surface roughness (Ra) of Vitremer in saliva media over 10 periods of time after the baseline values. There was a non-significant positive association (p = 0.676) between the Ra of Vitremer and its immersion in saliva media over a one year period. For every change in unit time, the slope was positive by (0.000143).

4.2.3.2. Changes in the Ra values of Activa bioactive restorative over a period of one year

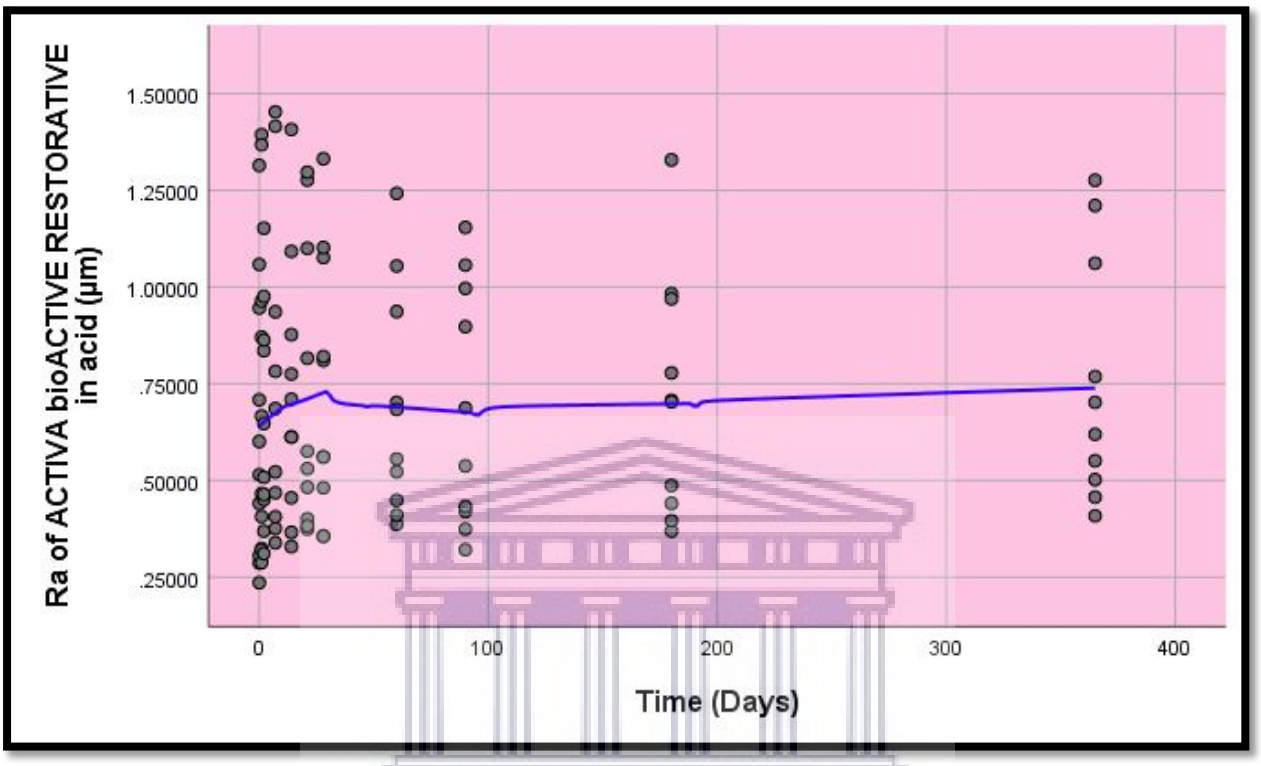


Figure (4.15): The surface roughness (Ra) of Activa material in acid media over 10 periods of time after the baseline values. There was a non-significant positive association (p = 0.633) between the Ra of Activa and its immersion in acidic media over a period of one year. For every change in unit time, the slope was positive by (0.000142).

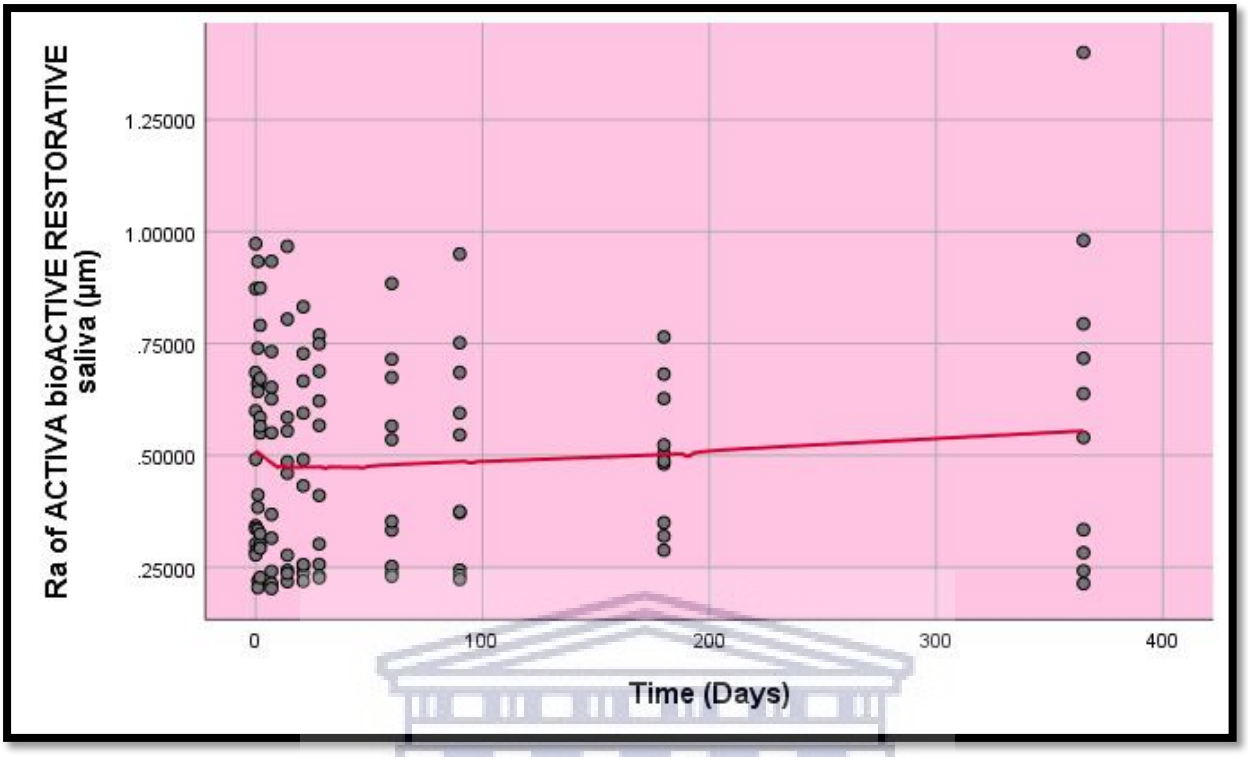


Figure (4.16): The surface roughness (Ra) of Activa in saliva media over 10 periods of time after the baseline values. There was a non-significant positive association (p = 0.201) between the Ra of Activa and its immersion in saliva media over a period of one year. For every change in unit time, the slope was positive by (0.000276).

4.2.3.3. Changes in the Ra values of Cention N over a period of one year

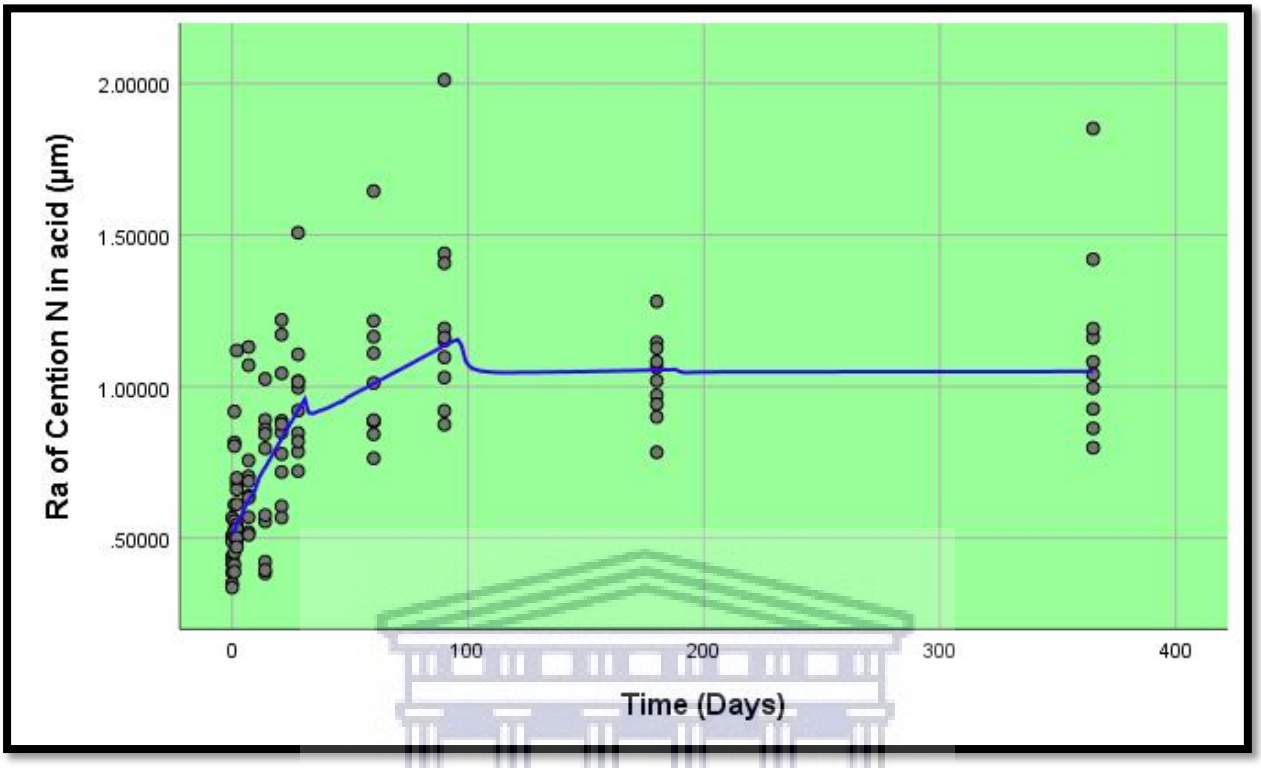


Figure (4.17): The surface roughness (Ra) of Cention N in acid media over 10 periods of time after the baseline values. There was a significant positive correlation (p = 0.000) between the Ra of Cention N and a period of one year in acid media. For every change in unit time, the slope was positive by (0.001).

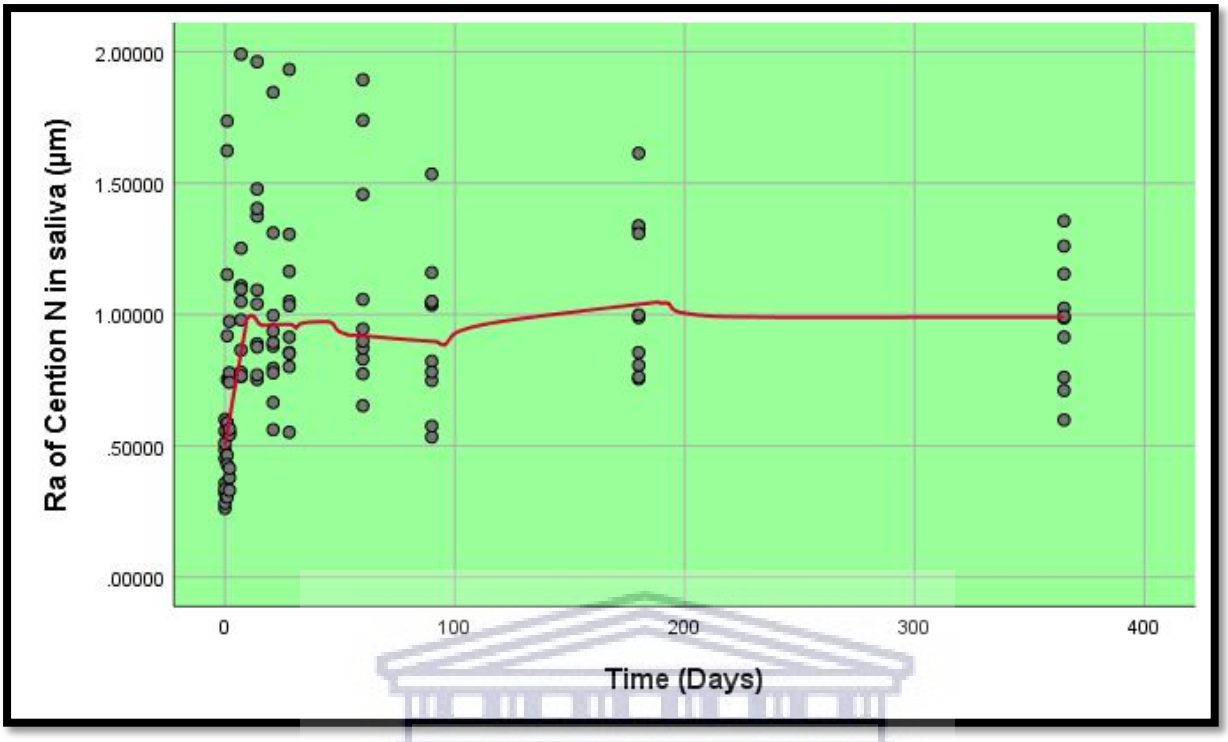


Figure (4.18): The surface roughness (Ra) of Cention N in saliva media over 10 periods of time after the baseline values. There was a non-significant positive correlation (p = 0.154) between the Ra of Cention N and a period of one year (0.001). For every change in unit time, the slope was positive by (0.001).

Table (4.2): Summarizes the materials that showed significant association of the studied variables after one year of immersion.

	Acidic Media			Saliva Media		
	Weight	Height	Ra	Weight	Height	Ra
Vitremer	Significant negative	Significant negative	Significant positive	Significant positive	-	-
Activa	-	-	-	-	-	-
Cention N	-	-	Significant positive	-	-	-

4.3. Correlation between the studied variables within the same material

In order to correlate the variables within each material, a non-parametric two-tailed correlation was used. This was done by means of a Spearman's test on a bi-variate level. The interpretation of the results was based on taking the reading above the diagonal line from the SPSS output.

4.3.1. Vitremer

Table (4.3) below showed the correlation between the weight (g), height (µm) and surface roughness (µm) of the Vitremer. In *acidic media*, there was a significant positive correlation between the weight of the Vitremer in acidic media and the height; as the height decreased, the weight also decreased.

On the other hand, there was a significant negative correlation between the weight of the Vitremer and the surface roughness; signifying that as the weight decreased, the surface roughness increased and the height decreased.

In saliva media, there was a significant positive correlation between the weight and height. On the other hand, there was a significant negative correlation between the height of Vitremer and the surface roughness. Thus, as the weight increased the height also increased but the surface roughness decreased.

Table (4.3): The correlation values between the variables for Vitremer in both acid and saliva media.* Means correlation is significant at the 0.05 level (2-tailed).

Vitremer (Correlation)	Height in acid	Surface roughness in acid	Height in saliva	Surface roughness in saliva (Ra)
Weight in acid	0.535*	-0.459*	-	-
Height in acid	-	-	-	-
Weight in Saliva	-	-	0.834*	-
Height in saliva	-	-	-	- 0.297*

4.3.2. Activa Bioactive Restorative

Table (4.4) below, showed the correlation between the weight (g), height (µm) and surface roughness (µm) of the Activa. With regard *to acidic media*, there was a significant positive correlation between the weight of the Activa and the surface roughness. Hence, as the weight increased the surface roughness also increased. Likewise, the same correlation was applied between weight and height. In addition, as the height increased, the surface roughness also increased. *In saliva media*, there was a positive correlation between the weight and height of Activa.

Table (4.4): The non-parametric correlation values between the variables in Activa in both acid and saliva media.* Means correlation is significant at the 0.05 level (2-tailed).

Activa bioactive restorative (Correlation)	Height in acid	Surface roughness in acid	Height in saliva	Surface roughness in saliva (Ra)
Weight in acid	0.529*	0.362*	-	-
Height in acid		0.722*	-	-
Weight in Saliva	-	-	0.750*	-

4.3.3. Cention N

Table (4.5) below, shows the correlation between the weight, height and surface roughness of Cention N. Regarding *acidic media* specifically, there was a significant positive correlation between the weight and height of Cention N in acidic media. Hence, as the height increased, the weight also increased.

In *saliva media*, there was a positive correlation between the weight and height of Cention N as well. On the other hand, there was a significant negative correlation between the height of Cention N and the surface roughness. The same significant negative correlation is applied to the weight and surface roughness. Therefore, as the weight increased, the height increased and the surface roughness decreased.

Table (4.5): The non-parametric correlation values between the variables in Cention N in both acid and saliva media.* Means correlation is significant at the 0.05 level (2-tailed).

Cention N (Correlation)	Height in acid	Surface roughness in acid	Height in saliva	Surface roughness in saliva (Ra)
Weight in acid	0.878*	-	-	-
Weight in Saliva	-	-	0.922*	-0.242*
Height in saliva	-	-	-	-0.266*

4.4. Comparison between different materials within the same media

The comparison between the three materials was done using the Kruskal-Wallis test. The Kruskal-Wallis test was used due to the fact that the data is not normally distributed. If the result of the test showed significance in one of the parameters, the Mann-Whitney test was used for detecting the exact significance which occurred between the two groups of materials.

4.4.1. Comparison between the materials in acid media

The reason behind the use of the Kruskal-Wallis test is to measure the difference for the skewed data. The test was applied at each point of time (was done in 10 periods of time). The Mann-Whitney was used to differentiate the significance of variables between the materials. After that, the main rank had been used in order to determine which variable is higher and which is lower. For each period of time, if the significance was higher than 0.05, the day was neglected in the comparison.

For the weight in acid the results were summarized in **Table (4.6) below**. The weight variable showed a significant difference between the three materials at each measurement time point (p = 0.000). The result of the Mann-Whitney test showed that the p-value was the same from day one up to day 60 of immersion in acidic media. After analyzing the main rank, Cention N was found to be significantly higher than Vitremer,

and Vitremer was found to be significantly higher than Activa. Furthermore, Cention N was found to be significantly higher than Activa. This ranking was applied to the weight of the specimens in acidic media in day 1, day 2, day 7, day 14, day 21, day 28, day 60 (Cention N > Vitremer > Activa).

However, after completion of three months (day 90) up to one year, there was a slight change in the results. Despite the fact that there was a significant difference between the three materials (p = 0.000), the difference became insignificant when it came to the comparison between the weight of the Vitremer and Activa in particular. Through the use of the main rank, Cention N was found to be statistically higher in weight than Vitremer as well as Activa. Yet, this difference in weight between Activa and Vitremer was not statistically significant (Cention N > Vitremer) ≥ Activa. This ranking was applied to the weight of the specimens in acidic media on day 90, day 180 and day 365.

Table (4.6): The statistical significance when the three materials were compared to each other in terms of weight in acidic media.

	Difference in days with reference to D0	*p*-value	Material	*p*-values for Mann-Whitney test
Significant weight results in acid media through the use of Kruskal Wallis test	D1-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.001
			Activa and Cention N	0.000
	D2-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.002
			Activa and Cention N	0.000
	D7-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.001

(n = 10) the same samples had been used throughout the study			Activa and Cention N	0.001
	D14-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.000
			Activa and Cention N	0.000
	D21-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.000
			Activa and Cention N	0.000
	D28-D0	0.000	Vitremer and Activa	0.001
			Vitremer and Cention N	0.000
			Activa and Cention N	0.000
	D60-D0	0.000	Vitremer and Activa	0.007
			Vitremer and Cention N	0.000
			Activa and Cention N	0.000
	D90-D0	0.000	Vitremer and Activa	-
			Vitremer and Cention N	0.000
			Activa and Cention N	0.000
	D180-D0	0.000	Vitremer and Activa	-
			Vitremer and Cention N	0.000
			Activa and Cention N	0.000
	D365-D0	0.000	Vitremer and Activa	-
			Vitremer and Cention N	0.000
			Activa and Cention N	0.000

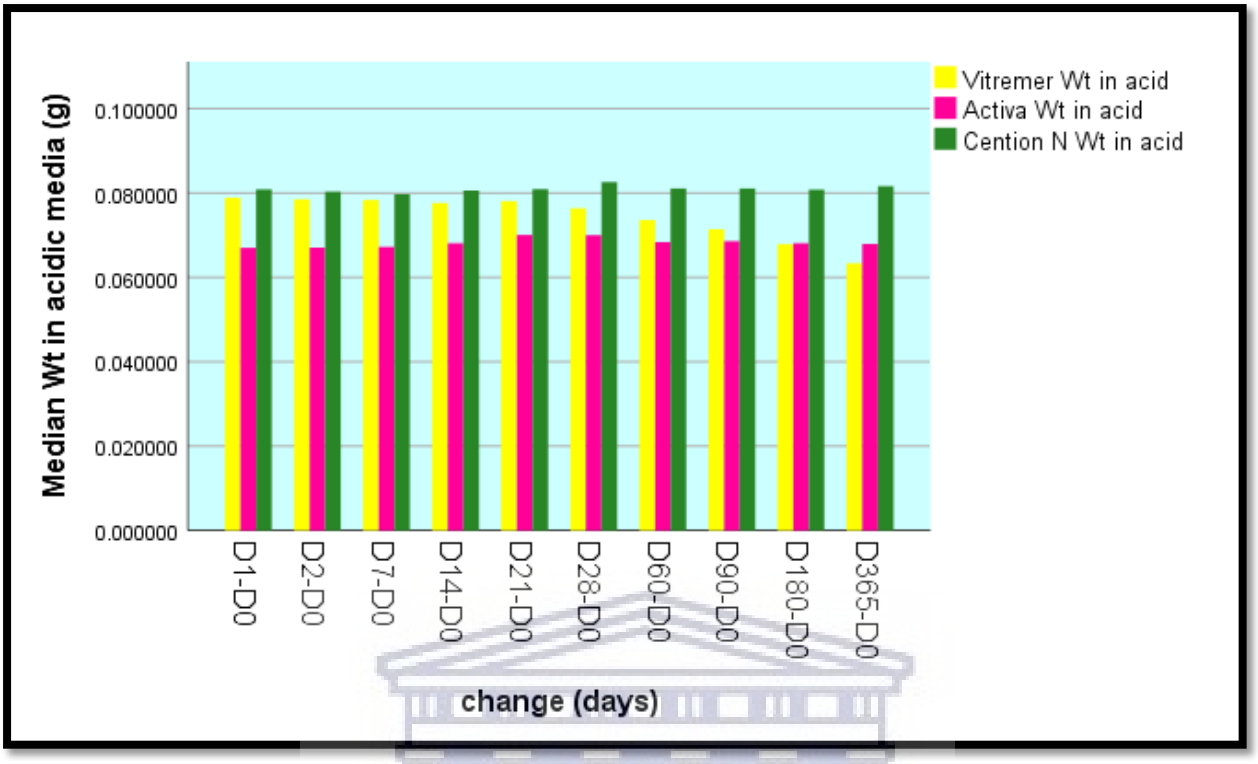


Figure (4.19): Description of the change in weight between the three materials in acidic media through the use of the median.

On the other hand, the comparison between the three materials in terms of height showed that there was an insignificant change in height in acidic media with reference to day zero. This outcome had been noticed in day 1, day 2, day 7, day 14, day 21, day 28, day 60, day 90 and day 180. However, only in day 365, there was a significant difference between the materials in term of height in acidic media (p = 0.048). In particular, there was a significant difference only between the height of Vitremer and Activa (p = 0.016). This significance had been translated in the main rank as Activa was significantly higher in height than Vitremer on day 365. Furthermore, Cention N was found to be higher on day 365 than Activa and Vitremer, but this difference was not statistically significant. Hence the ranking could be summarized as (Cention N ≥ Activa > Vitremer) and this ranking took into consideration that Cention N ≥ Vitremer.

Table (4.7): The statistical significance when the three materials were compared to each other in term of height in acidic media.

Significant height results in acid media through the use of Kruskal Wallis test (n = 10) the same samples had been used throughout the study	Difference in days with reference to D0	*p*-value	Material	*p*-values for Mann-Whitney test
	D365-D0	0.048	Vitremer and Activa	0.016
			Vitremer and Cention N	-
			Activa and Cention N	-

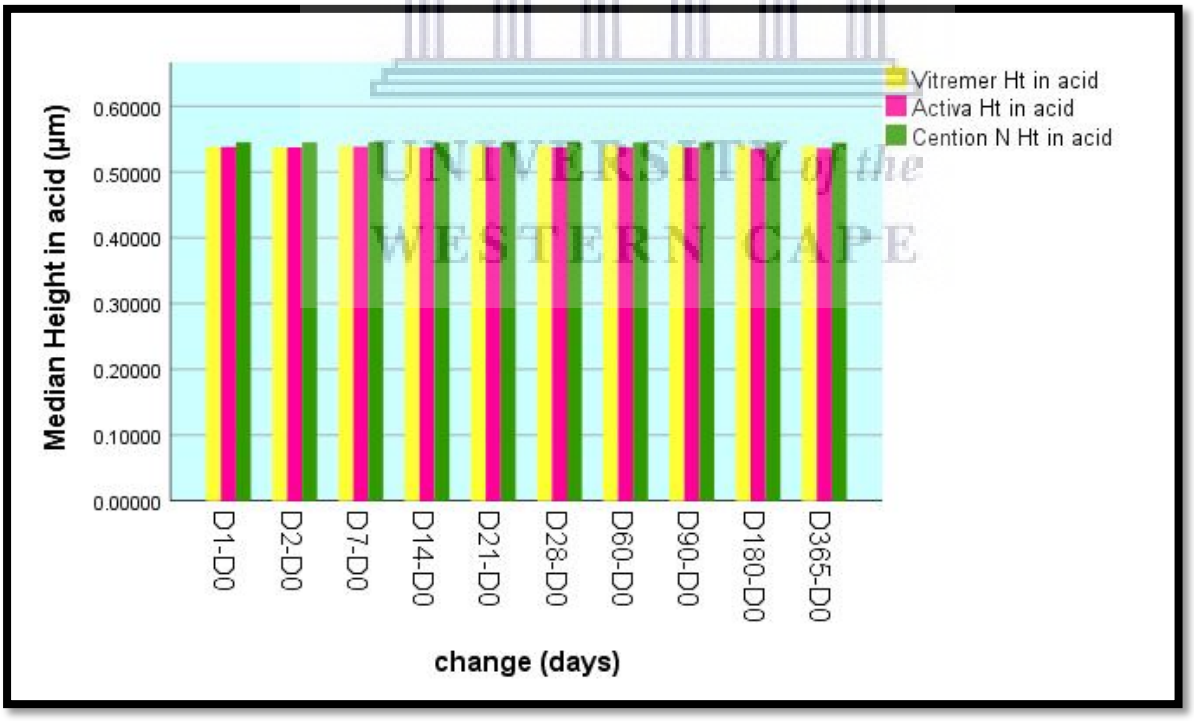


Figure (4.20): Description of the changes in height between the three materials in acidic media through the use of the median.

Regarding the surface roughness, the difference between the materials was only found to be significant between the following days: day 1, day 7, day 14, day 180 and day 365 with reference to day zero. In particular, this difference was significant only between Vitremer and Cention N during the early days of immersion: day 1, day 7 and day 14. When analyzing the main rank, the surface roughness of the Vitremer was found to be significantly higher than for Cention N. Vitremer's surface roughness was higher than Activa as well. However, this difference in surface roughness was not statistically significant. Hence, in day one the material ranks were as follows: (Vitremer ≥ Activa > Cention N). Following the same manner on day 7 and day 14, Vitremer had a significantly higher surface roughness value than Cention N. Furthermore, Vitremer, on day 7 and day 14, was reported to have higher values than Activa as well, but this difference was not statistically significant. When comparing Activa and Cention N, Activa had higher surface roughness than Cention N, but this difference was also of no significance on day 7 and day 14 in relation to the baseline. Hence the main rank could be summarized as follow: (Vitremer ≥ Activa ≥ Cention N) taking into consideration that V > C. After that, no significant difference was detected between the materials on day 21, 28, 60 and 90. However, on day 180, as the material aged in the saliva media, a significant difference (p = 0.01) started showing between the three materials with changes in the ranking. Although Vitremer was reported to have significantly higher Ra than both Cention N and Activa, Cention N was found to have higher surface roughness than Activa. However, this difference between Cention N and Activa was found to be insignificant as shown in **Table (4.8)** below. Therefore, the ranking on day 180 could be summarized as follow: Vitremer > Cention N ≥ Activa. This ranking is also detected between the materials on day 365 but the (p = 0.158) for the Kruskal-Wallis test was found to be insignificant.

Table (4.8): The statistical significance when the three materials compared to each other in terms of surface roughness in acidic media.

	Difference in days with reference to D0	*p*-value	Material	*p*-values for Mann-Whitney test
Significant surface roughness (Ra) results in acidic media through the use of Kruskal Wallis test (n = 10) the same samples had been used throughout the study	D1-D0	0.037	Vitremer and Activa	-
			Vitremer and Cention N	0.02
			Activa and Cention N	-
	D7-D0	0.044	Vitremer and Activa	-
			Vitremer and Cention N	0.005
			Activa and Cention N	-
	D14-D0	0.022	Vitremer and Activa	-
			Vitremer and Cention N	0.003
			Activa and Cention N	-
	D180-D0	0.01	Vitremer and Activa	0.005
			Vitremer and Cention N	0.000
			Activa and Cention N	-

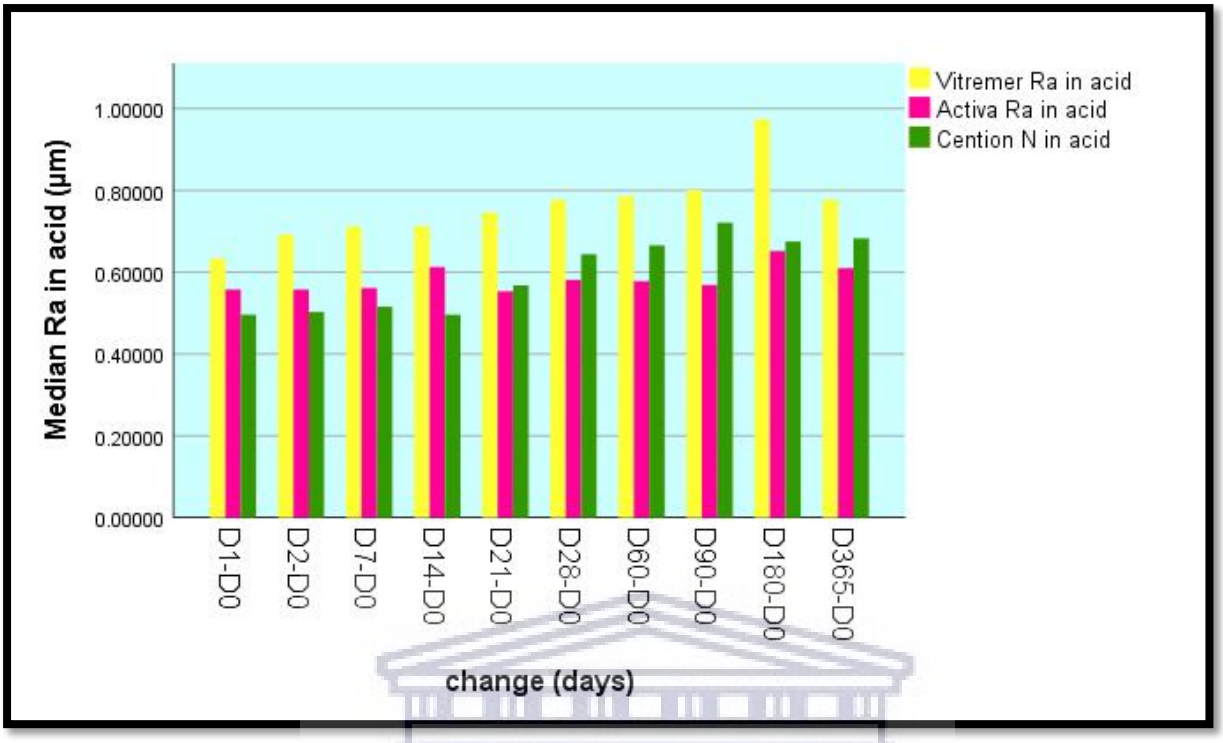


Figure (4.21): Description of the changes in surface roughness between the three materials in acidic media through the use of the median.

4.4.2. Comparison between the materials in saliva media

When the studied materials were compared to each other in saliva media, the weight variable was the only variable that showed a significant difference (p = 0.000). This significance was detected at each point of time during the whole study period. Furthermore, between the materials the Mann-Whitney test showed that on day 1, day 2, day 7, day 14, day 21, day 28, day 60, day 90 and day 180 Cention N was reported to be significantly higher in weight than both Vitremer and Activa. In addition, Vitremer was reported to be significantly higher in weight than Activa. Hence the ranking in the above mentioned data was reported as follows: (Cention N > Vitremer > Activa). However, as the materials aged in the artificial saliva, as shown on day 365, Cention N reported to have the highest weight in artificial saliva in comparison to Vitremer and Activa. The difference became insignificant between Vitremer and Cention N particularly. Hence the ranking on day 365 could be summarized as follows: (Cention N ≥ Vitremer > Activa) considering that Cention N > Activa. **Table (4.9)** below, is presented the significance of the three materials among the 10 periods of time.

Table (4.9): The statistical significance when the three materials were compared to each other in terms of weight in the saliva media.

	Difference in days with reference to D0	*p*-value	Material	*p*-values for Mann-Whitney test
Significant weight results in saliva media through the use of Kruskal Wallis test (n = 10) the same samples were used throughout the study	D1-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.001
			Activa and Cention N	0.000
	D2-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.000
			Activa and Cention N	0.000
	D7-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.008
			Activa and Cention N	0.000
	D14-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.001
			Activa and Cention N	0.000
	D21-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.003
			Activa and Cention N	0.000
	D28-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.004

			Activa and Cention N	0.000
	D60-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.003
			Activa and Cention N	0.000
	D90-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.002
			Activa and Cention N	0.000
	D180-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	0.01
			Activa and Cention N	0.000
	D365-D0	0.000	Vitremer and Activa	0.000
			Vitremer and Cention N	-
			Activa and Cention N	0.000

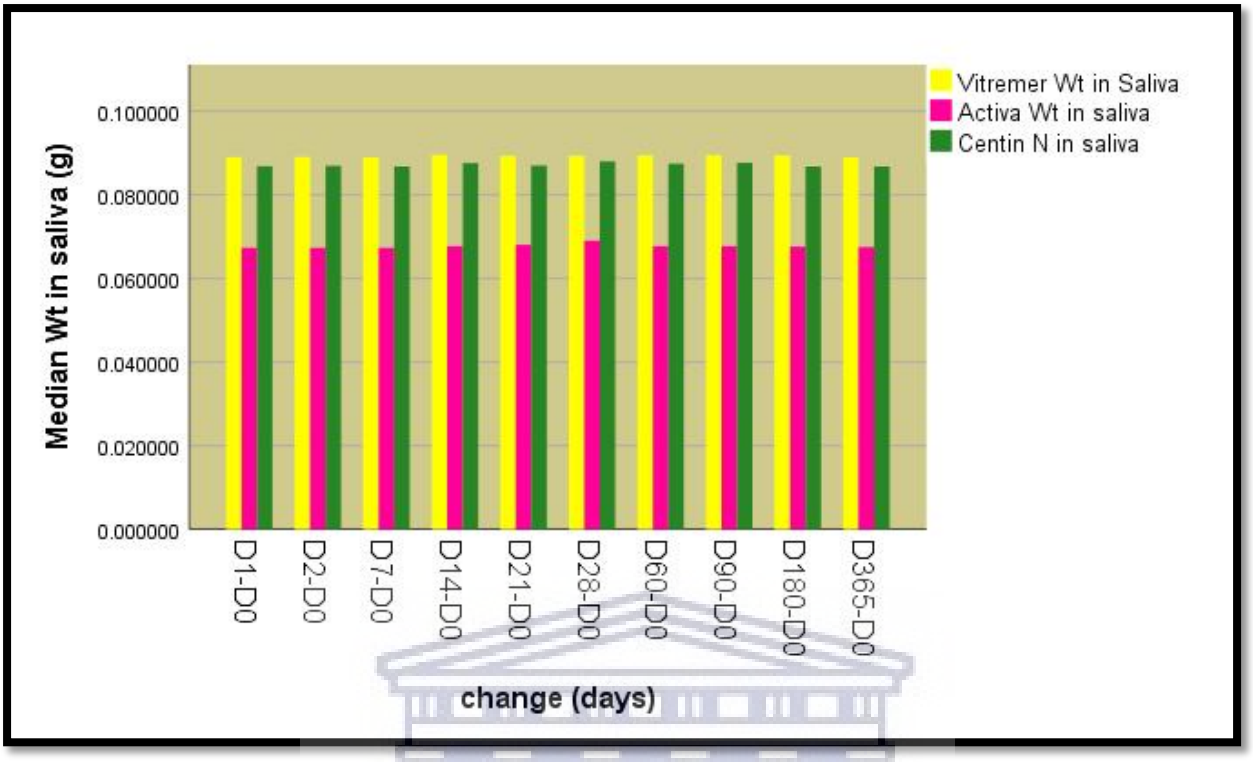


Figure (4.22): Description of the changes in weight between the three materials in saliva media through the use of the median.

On the other hand, the results of the comparison of height showed that there was not a statistical significance in terms of height when the three materials were compared to each other. Throughout the 10 periods of time, Cention N ranked the highest in height followed by Activa. Vitremer was reported to have the lowest height among the three materials. This is illustrated in **Figure (4.23)** below. The pattern of fluctuation in the graph of Ra measurements was the same in the descriptive statistics. The descriptive statistics used the median due to the fact that the data was not normally distributed.

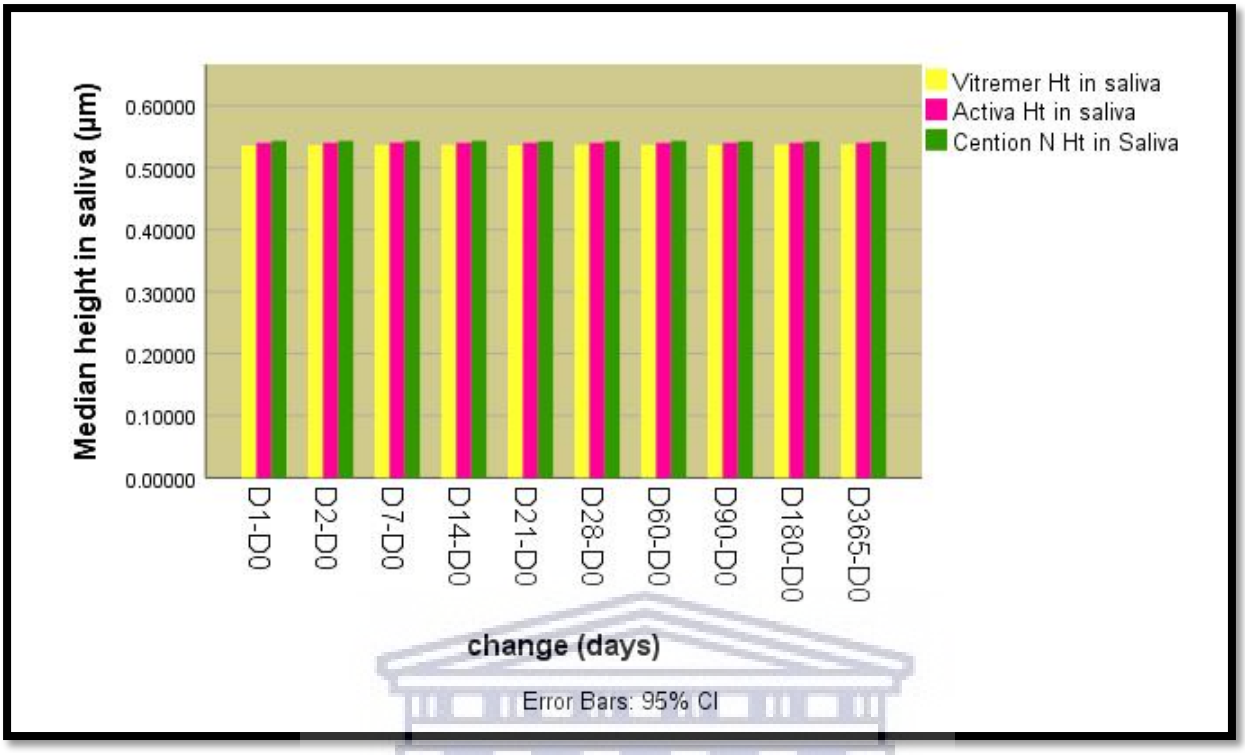


Figure (4.23): Description of the changes in height between the three materials in saliva media through the use of the median.

The Ra in artificial saliva media showed that there was not a significant difference between the materials after measuring them in 10 periods of time as well. In relation to the baseline, Activa always reported to have the lowest surface roughness except on day 2 when Cention N was reported to be the lowest. On the other hand, when looking at the comparison between Vitremer and Cention N, fluctuations in the results were noticed. Vitremer had the highest surface roughness on day 1, day 2, day 21, day 60 and day 90. On the other hand, on day 7, 14, 28, 180 and 365, Cention N ranked the highest in terms of surface roughness.

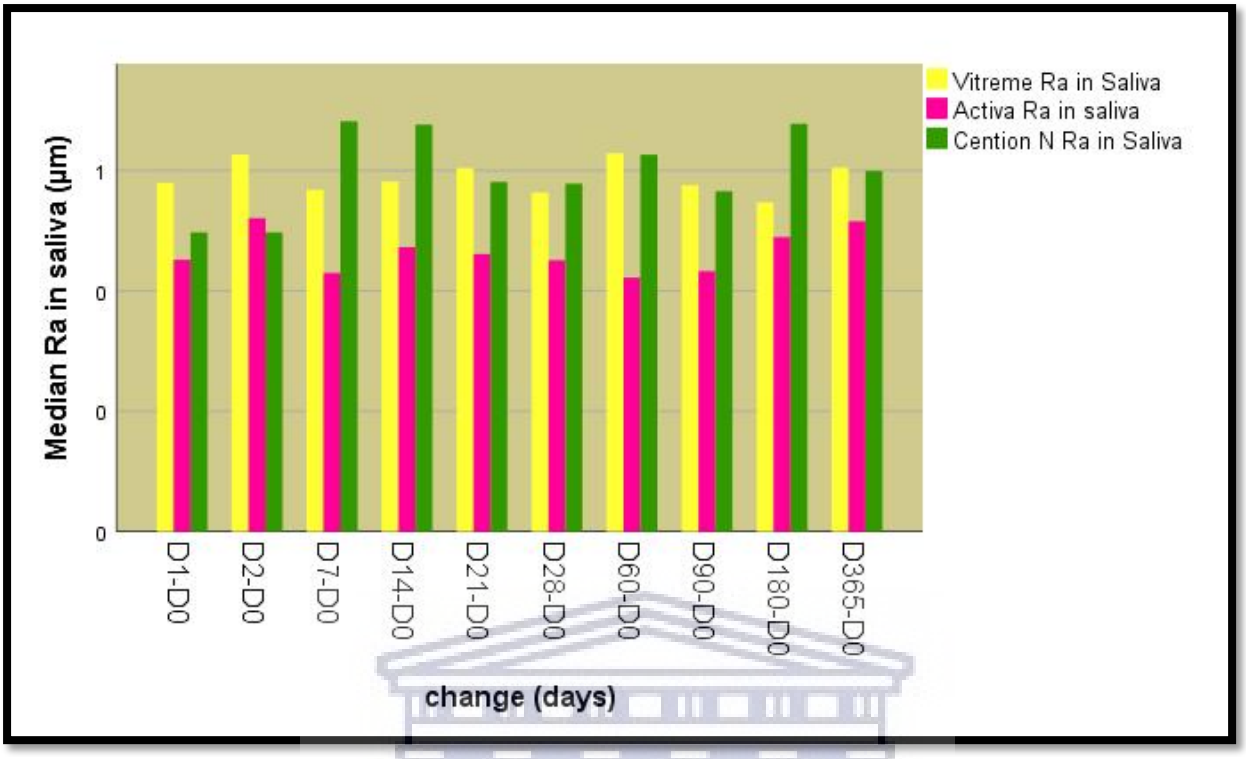


Figure (4.24): Description of the changes in surface roughness between the three materials in saliva media through the use of the median.

4.5. Result of fluoride release when the materials are immersed in de-ionized water

As stated by the manufacturer, fluoride measurement should be done according to the following steps; the first step is to reach an acceptable pH of the measured solution. In order to determine the level of fluoride for each solution, it is important to determine the pH of the solution. The rationale for determination of the pH before starting fluoride measurement is to prevent a reaction of the electrode with the solution and consequently, if the pH is in an acceptable range, measuring the electrode potential (mV) for every RMGIC-diluent is performed through the use of calibrated fluoride selective electrode.

According to the manufacturers, other factors that could affect the accuracy of fluoride measurement in addition to the pH are: the temperature, presence of noise in the lab, or presence of some anions in the solutions that could interfere with the accuracy of the recorded values using a fluoride electrode. The interference is directly related to the

presence of hydroxide ions, especially if the percentage of these ions is higher than 10% of the total percentage of fluoride present in the solution (Orion Research Incorporated, 2016). Likewise, other anions could indirectly confound the fluoride reading through making the solution more alkaline such as phosphate (PO_3^{-3}) or carbonate (CO_3^{-2}) in the solution. Therefore, it is important to adjust the pH through the addition of chelating buffer agents; TISAB II or TISAB III to buffer the pH of the investigated solution to reach a specific level (5 - 5.5). If TISAB III is intended to be used for buffering, the pH should be in the range of (8.5).

In the present study, the following TISAB II, III and IV were prepared. The collected data for fluoride showed that each material had five collected solutions and the volume of each solution was 5 ml. For every studied material, a random specimen jar was used from day 1 samples to measure the pH. A blank solution from de-ionized water was collected during each period of time and the outcome of the result was recorded as follows:

- The pH of the blank solution in day 1 was equal to 5.53

Table (4.10): Shows the pH of the collected solutions after 24 hrs immersion period in de-ionized water with regard to TISAB II.

Day 1	pH when TISAB II added	pH without TISAB II
Vitremer	7.74	8.94
Activa	7.73	8.95
Cention N	7.74	8.95

Table (4.11): Shows the pH of the collected solutions after 24 hrs immersion period in de-ionized water with regard to TISAB III.

Day 1	pH when TISAB III added	pH without TISAB III
Vitremer	4.81	5.87
Activa	4.83	5.76
Cention N	4.83	6.25

The fluoride experiment was actually not conducted although the diluents were made on the day of testing and the pH was measured initially. However, after that, when TISAB II and III were added, the solutions did not show an acceptable record for pH in order to carry on to the next step of fluoride measurement. A person could speculate that the assessment of fluoride was hindered because the pH values of the collected solutions were out of the acceptable range for fluoride measurement. In particular, when TISAB II was added to the solutions of the three materials, all the pH values of the solutions were above 7.7 which exceeded the upper limit (5.5) for fluoride measurement. Furthermore, the solutions of all of the three materials were alkaline which certainly would confound the fluoride reading.

On the other hand, when TISAB III was added to the solutions, all the solutions recorded a pH of around 4.83 which is lower than the lower limit for the acceptable range for fluoride measurement (5) which could affect the fluoride probe or lead to recording of an internally invalid results.

4.6. Qualitative analysis (SEM analysis)

SEM images were used in order to qualitatively assess the surfaces of the tested materials through studying the surface at a higher magnification and hence aid in the interpretation of the roughness variable. Use of the SEM showed that the three materials varied widely in the nature of the filler particle, shape and size. The SEM showed that Vitremer generally had a larger filler size in relation to Cention N and Activa. Activa showed a relatively smaller particle size.

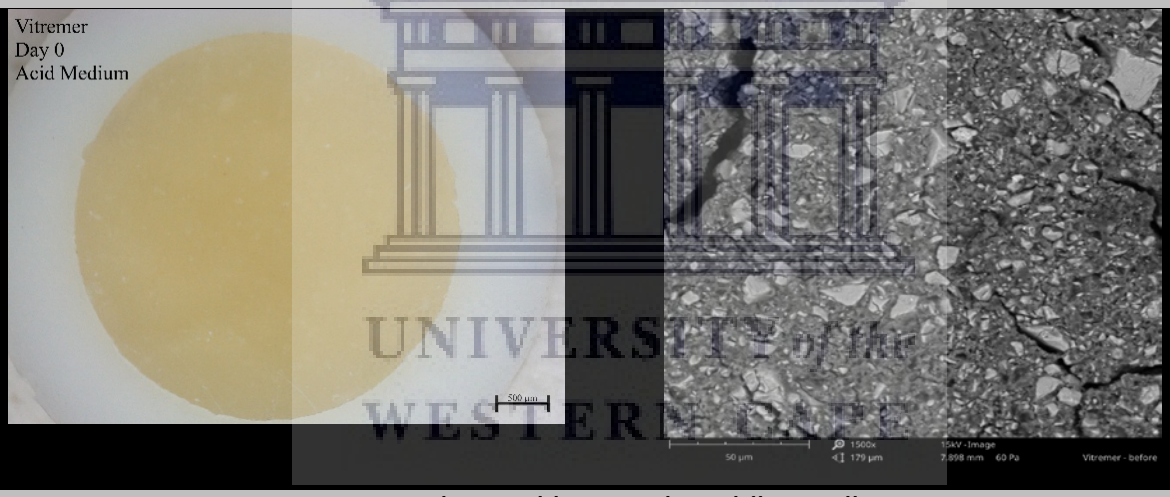
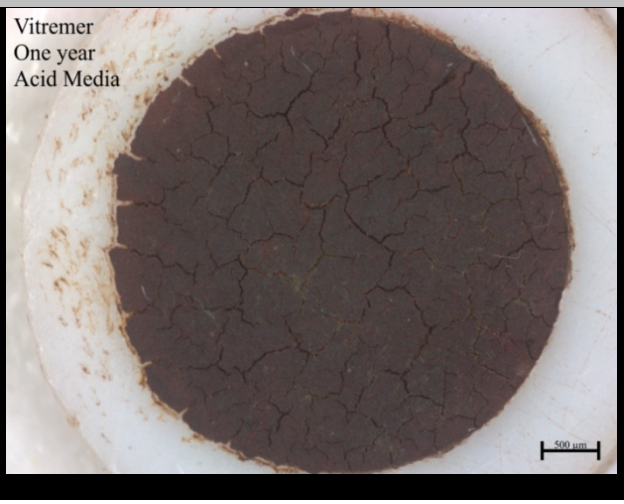
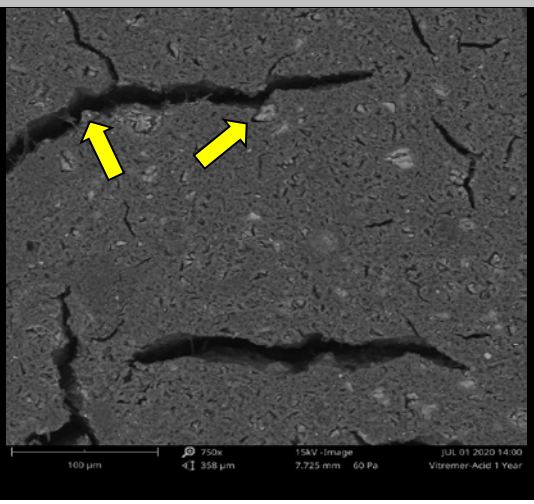
4.6.1. Vitremer under SEM

Figure (4.25) below shows the stereo-microscope images of Vitremer pre-experimentally and post-experimentally in the acidic and saliva media respectively. These three images are matched with the SEM images at 1500X magnification.

The pre-experimental SEM image of Vitremer showed moderate homogenous filler distribution of the fillers on the surface, with good integration between the fillers and matrix, although some cracks were present on the surface. However, the particles were clearly integrated on the surface. On the other hand, the post-experimental SEM images

in acidic media showed the surface to be heavily cracked which led to exposure of the inner surface. On the other hand, the post-experimental Vitremer sample that was immersed in saliva had less cracks when compared to the image of acidic media. The filler particle dissolution was clear on the post-experimental image for the saliva sample compared to the pre-procedure for the saliva sample. This illustrates the influence of the acid on the dissolution of the filler particles.

Furthermore the saliva sample showed that the particles on the surface became more prominent in relation to the pre-experimental image.

Vitremer	
Stereo-microscope images	Scanning electron microscope images
Pre-experimental image (Before immersion)	
	
Post-experimental images in acidic media	
	

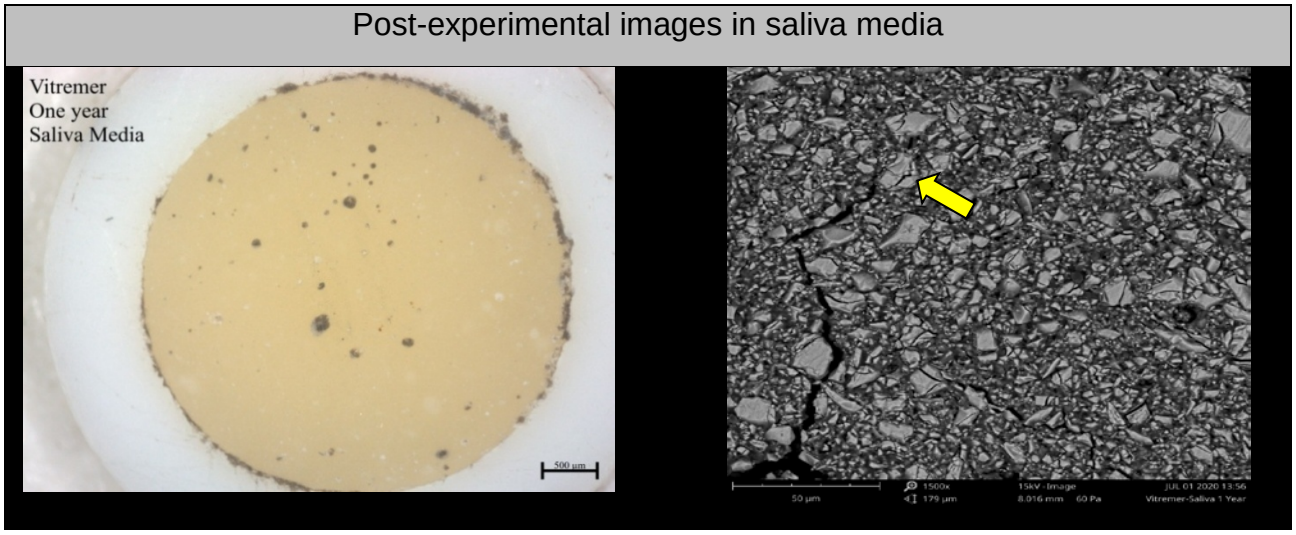


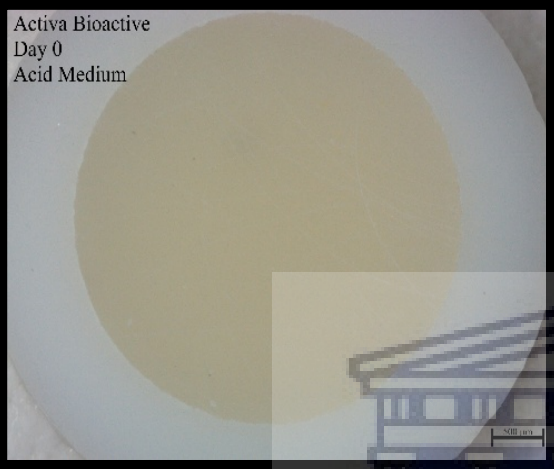
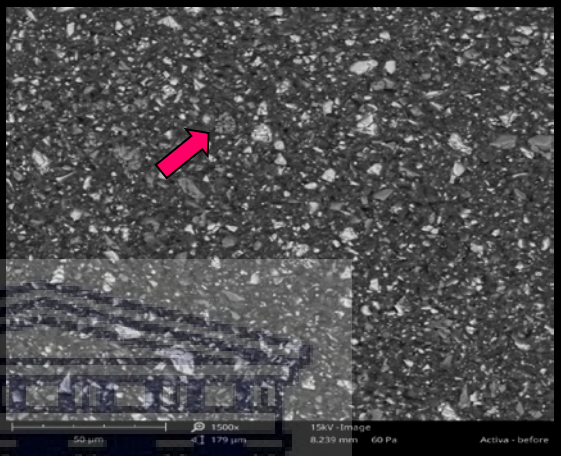
Figure (4.25): The pre and post-experimental stereo-microscope and SEM images of Vitremer. The yellow arrows show projection of fillers around cracks in post-experimental images.

4.6.2. Activa Bioactive Restorative under SEM

Figure (4.26) below shows the stereo-microscope images of Activa pre-experimentally and post-experimentally in the acidic and saliva media respectively.

Under the SEM, the pre-experimental image of Activa showed that the surface was homogenous in terms of filler distribution. Furthermore, it showed an even distribution of the filler particles. Furthermore, this image showed that the material had the smallest particle size of the three materials. There was also variation in the size of the particles. The shape of the particles was shown to be more spherical pre-experimentally than irregular. However, it became more irregular post-experimentally in the saliva sample. This could be related to the fact that interaction of saliva with the surface of Activa made the fillers more pronounced. Hence, their real shape emerged to the surface.

This change in the backscattering property could be related to the loss of some particles or due to the presence of porous fillers. However, the present study could not conclude whether the shape of the pores in the SEM actually represents the location of the lost fillers, or are they due to an increase in porosity that leads to changes in the contrast of the material as a result of the release of ions from the fillers.

Activa bioactive restorative	
Stereo-microscope images	Scanning electron microscope images
Pre-experimental images (Before immersion)	
	
Post-experimental images in acidic media	
	
Post-experimental images in saliva media	

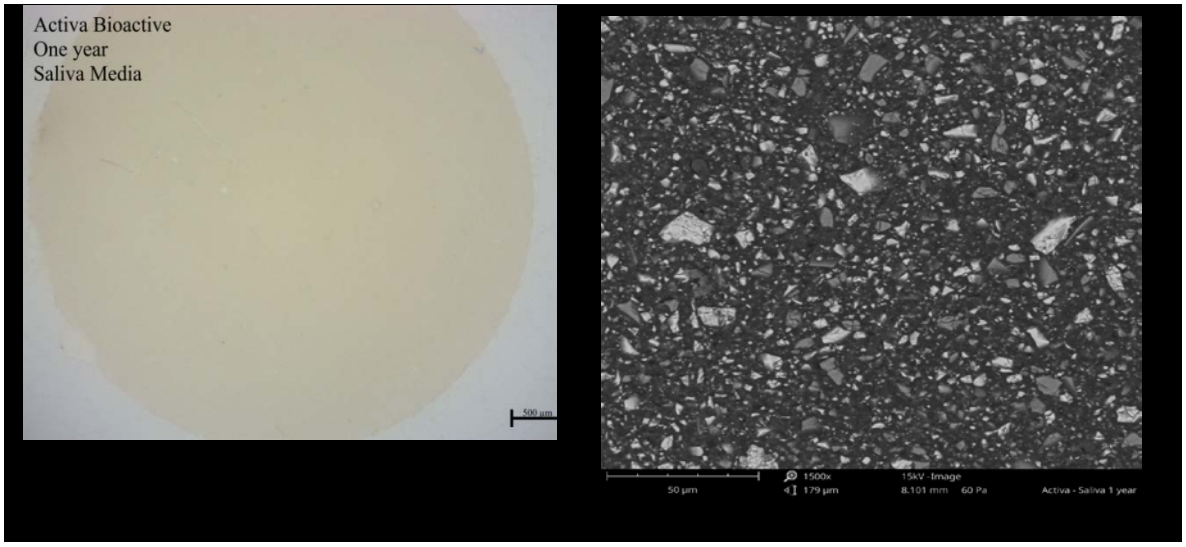


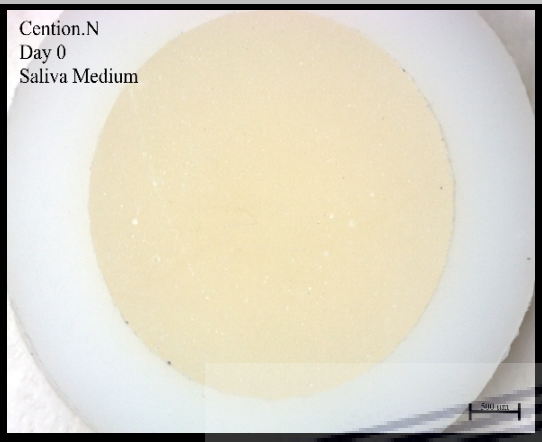
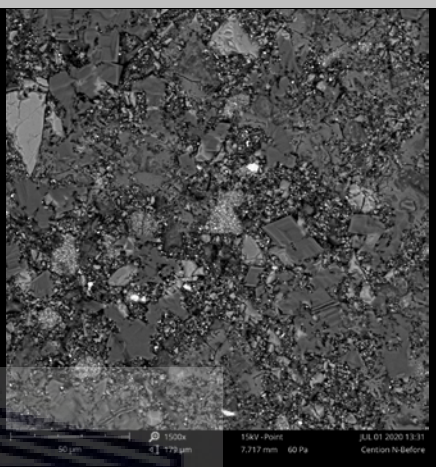
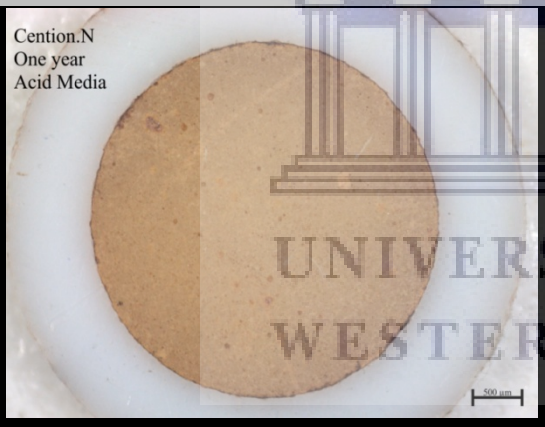
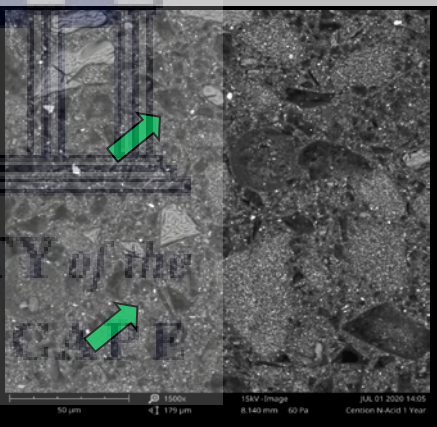
Figure (4.26): The pre and post-experimental stereo-microscope and SEM images of Activa. The pink arrows show change in the back scattering of fillers post-experimentally in acid media. Cracks were absent from all images.

4.6.3. Cention N under SEM

Figure (4.27) below shows the stereo-microscope images of Cention N pre-experimentally and post-experimentally in the acidic and saliva media respectively.

The pre-experimental image demonstrated Cention N to have the greatest variation in filler size and shape with the least volume loss from the matrix as depicted in the SEM images. The SEM image of Cention N showed that there were filler particles present on the surface due to the difference in their backscattering property.

On the other hand, the post-experimental image showed loss of a particular filler particle as illustrated by the green arrows. This filler loss from Cention N affected the Ra. The Ra results emulated the change in Ra in the acidic media compared to the saliva media. In both post-experimental images, there were no cracks detected on the surface in the acid and saliva samples.

Cention N	
Stereo-microscope images	SEM images
Pre-experimental images (Before immersion)	
	
Post-experimental images in acidic media	
	
Post-experimental in saliva media	

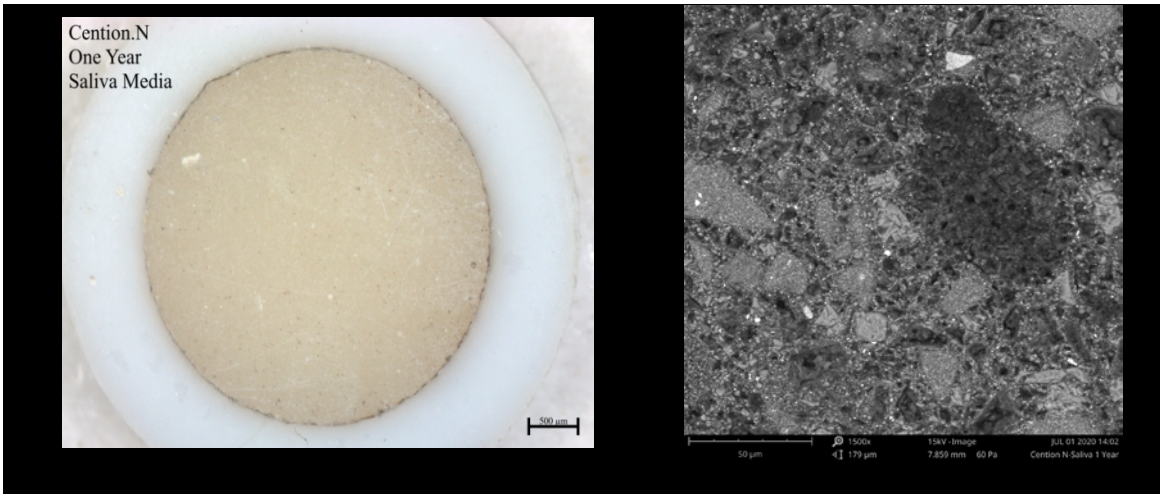


Figure (4.27): The pre and post-experimental stereo-microscope and SEM images of Cention N. The green arrows show change in the back scattering of fillers post-experimentally in acid media. Cracks were absent from all images.

CHAPTER V: DISCUSSION

5.1. Association of weight and height changes over a one year period (going through ten periods of time)

5.1.1. Association of Vitremer's weight and height changes

The findings of the present study showed that when Vitremer had been immersed in acidic media there was a significant negative association between weight and height after one year of immersion (p = 0.000) and (p = 0.007) respectively. This could probably be related to the cumulative erosive effect of acid on Vitremer samples over an extended period of time. The erosion is due to displacement of polyacrylic acid in Vitremer by lactic acid (Nicholson *et al.*, 1999). This led to significant weight reduction throughout the study. Furthermore, loss of weight could be explained by the dissolution of the matrix, peripheral to glass particles, hence the release of the HEMA component (Fúcio, *et al.*, 2008). Furthermore, this erosive effect of the acid is combined with hydrolysis of the cement (Cattani-Lorente *et al.*, 1994). However, this finding was found to be inconsistent with Şahmalı *et al.* (2003) who found that there was a total weight gain of 1.02% when Vitremer was immersed in lactic acid over a period of six weeks. Şahmalı *et al.* (2003) measured the weight after each week and found that there was a slight initial weight gain at the beginning of the study due to hydrolysis of the matrix followed by gradual weight loss due to the loss of fillers. The inconsistency found between the finding of Şahmalı *et al.* (2003) and the finding of the present study could be related to the shorter period of time in relation to the present study. Hence, Vitremer could have been in the phase of water sorption till the end of their study.

In addition, the findings of the present study are inconsistent with Nicholson *et al.* (1999) who found that there was weight gain in Vitremer specimens after immersing them into lactic acid for a period of one week (Nicholson *et al.*, 1999). However, it is important to mention that the major difference between the Nicholson *et al.* (1999) study and the present study was that the author used Vitremer luting cement with a PLR of 1.5: 1 which is less than the PLR of the restorative cement that is used in the present study

(2.5: 1). Reduction in the PLR would render HEMA more hydrophilic and hence lead to an increase in the sorption values (Yap, 1996). Furthermore, less filler particles make it more susceptible to dissolution. Dissolution of particles could explain why Nicholson *et al.* (1999) found that Vitremer luting increased the pH from 2.6 to (4.14 ± 0.04 SD) after one week. Lactic acid modifies the ion releasing property of Vitremer in order to neutralize the media during the acidic attack (Nicholson *et al.*, 1999). However, the Nicholson *et al.* (1999) study was conducted in a short period of time (limited to one week) compared to the present study.

However, as Vitremer aged in the acidic media, cumulative weight loss occurred as depicted in **Figure (4.1).** No long term study was found in the literature to compare the quantitative weight changes of Vitremer after a long period of immersion to the findings of the present study.

Lactic acid is the most commonly used acid in the *in vitro* studies to investigate the mechanical properties of Vitremer (Fano *et al*., 2004; Correr *et al*., 2012), because the lactic acid forms more than 80% of the total acids in the carious dentin in spite of the fact that the acid profile of the carious dentin varies and contains different types of acids (Hojo *et al.*, 1991; Hojo *et al.*, 1994; Nicholson, *et al.*, 1999). Moreover, the bacteria responsible for the dental caries are lactate producing cariogenic bacteria; lactobacilli and streptococci (Hojo *et al.*, 1994). Furthermore, it has been found that the effect of the *S.mutans* biofilm on the surface of the restoration was material dependent (Fucio *et al.*, 2008). Other major acids that have been found in the carious dentin are acetic acid and propionic acid (Hojo *et al.*, 1991; Nicholson, *et al.*, 1999). Furthermore, Featherstone & Rodgers (1981) found that mixing the lactic acid with acetic acid could have an increased demineralizing effect on the tooth surface (Featherstone. & Rodgers, 1981; Hojo *et al.*, 1994). Yet, these studies indicate that certain variables, such as the acid profile, concentration, and the pH could all have an effect on the RMGICs as investigated in the present study.

There is considerable variation in the literature about the formulation of acidic media used to measure the weight changes. Although most of the studies used lactic acid, the concentration and the pH of the media of Nicholson *et al*. (2.6) is closer to the pH of the

present study (around 3). On the other hand, Şahmalı *et al.* (1999) only reported the pH after one week of immersion without mentioning the baseline value as shown in **Table (5.1)** below. Both Nicholson *et al.* (1999) and Şahmalı *et al*. (2003) used lactic acid at a concentration of 0.02 mol/L which is lower than the concentration of lactic acid used in the present study.

Table (5.1): The reported studies with different formulations of acidic media solutions that were used to measure weight of Vitremer restorative dental material.

Author	Study title	Acid formulation	pH of the acidic media	Results
The present study	Comparative *in vitro* study of selective physical properties of Activa, Cention N and Vitremer	0.1 mol/L of mixture of lactic acid and sodium lactate	2.74	Total weight loss by 10.9% from the baseline (D0). The sequence of weight loss in relation to baseline in acidic media according to the periods of time was found as follows: day 1 showed slight increase (1.7%), followed by reduction in all following periods of time; day 2 (0.9%), day 7 (2.4%), day 14 (4.66%), day 21 (4.72%), day 28 (6.6%), day 60 (12.7%), day 90 (18.8%), day 180 (24.9%), day 365 (33.9%).
Şahmalı *et al*., 2003)	The interactions of tooth-colored dental restorative materials with aqueous lactic acid	2 ml of 0.02 mol^{-1} of lactic acid.	2.7 (measured after a week since immersion)	Weight gain of Vitremer by 1.02% after 6 weeks of immersion

Nicholson *et al*., 1999)	A preliminary study of the effect of glass ionomer and related dental cements on the pH of lactic acid storage solutions	8 cm^3 of 20 $mmol/dm^{-3}$ lactic acid solution	2.6	Increase in mass of Vitremer luting cement by the percentage of (3.52% ± 0.4 SD) after lactic acid immersion for one week.

On the other hand, the findings of the present study showed that when Vitremer had been immersed in artificial saliva media there was a significant positive association between the weight and immersion time of one year (p = 0.002). The slope was positive by (1.665 E^{-5}). Although this positive association was applied to the height as well, it was not significant (p = 0.177). The interaction of Vitremer with saliva was different from acid. This could be related to the interaction of chemical ions in artificial saliva that occurred in the lab such as the calcium, phosphate and chloride which matched the ions that were used by Nicholson (1997). The presence of these salts could lead to the absence of the well-defined concentration gradient that could inhibit the full release of the ionic elements of Vitremer to the artificial saliva media.

In the present study, the association of the weight of Vitremer and the immersion time over a period of one year in artificial saliva is presented in **Figure (5.1)**. In **Figure (5.1)**, the graph was divided into three phases:

- Phase I: Early steep period of weight gain.
- Phase II: Stationary period.
- Phase III: Late slight period of weight gain.

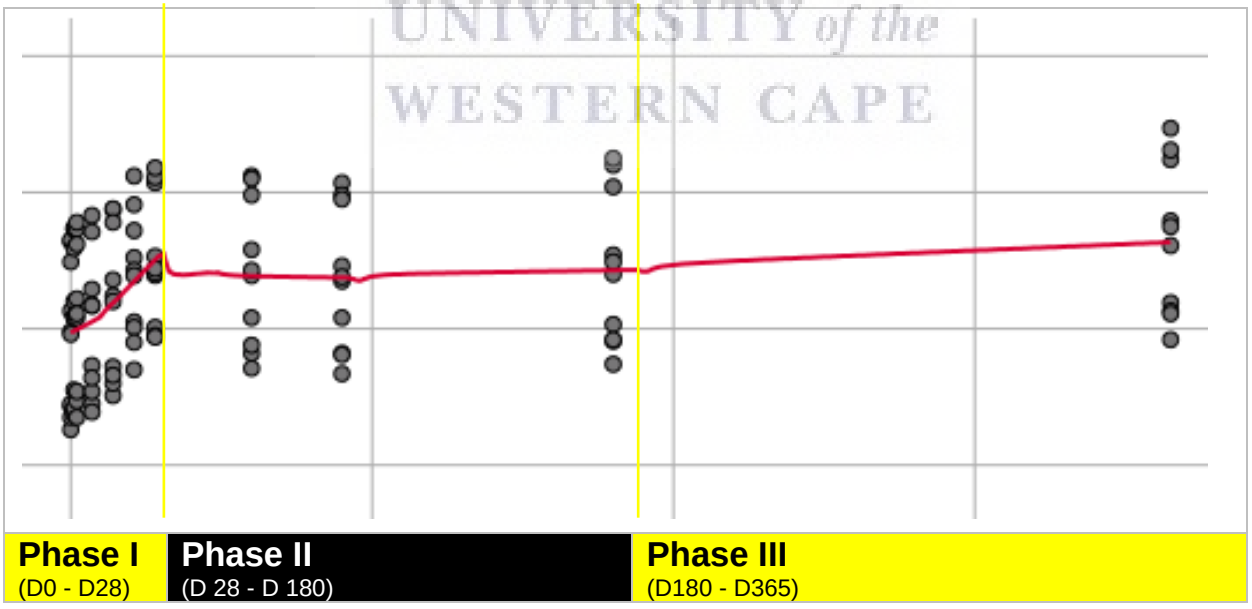


Figure (5.1): The phases of change in Vitremer's weight in saliva media.

The literature is discussed according to each phase.

- **Phase I: Early steep period of weight gain**

The present study showed a gradual increase in the percentages of the mean weight values till the end of the first month as follows; day 1 (1.2%), day 2 (1.3%), day 7 (0.7%), day 14 (2.9%), day 21 (4.98%), day 28 (6.6%). The early onset of weight gain could be justified by the water sorption (Nicholson, 1997; Iwami, *et al.*, 1998). The bulk of the literature mentioned that Vitremer absorbs the highest amount of water during the the first week (Nicholson, 1997; Iwami, *et al.*, 1998). However, the peak of water sorption in the current investigation was on day 28. The presence of hydrophilic HEMA in addition to the ongoing acid base reaction makes the polymer very flexible with greater heterogeneity of the hydro-gel structure of the polymer (Toledano *et al.*, 2003; Beriat. & Nalbant., 2009). Consequently, some conformational changes occur to the backbone of poly HEMA to form a compact coil that attracts water (Akashi *et al.*, 1999). This hydrophilic HEMA domain in the matrix could lead to the formation of a phase separation with a higher probability of micro-void formation (Nicolson, 1997; Akashi *et al.*, 1999). Furthermore, this softening effect could also be related to the lower degree of conversion of some monomers such as Bis-GMA and subsequent breakage of C=C double bond (Moszner *et al.*, 2008).

There are two theories which could explain the mechanism of water sorption; firstly, through the diffusion of water to micro-voids in order to interact with the matrix or secondly, a state in which water binds to hydrophilic compounds (Müller *et al.*, 2017). It was reported in the literature that the amount of water sorption of the RMGICs was higher than for the compomer and resin composite (Iwami, *et al.*, 1998). The literature review indicated that the RMGICs were hydrophilic material, hence, water sorption and dehydration could result in structural and dimensional changes (Kanchanavasita *et al.*, 1997; Iwami, *et al.*, 1998). Furthermore, it has been reported that within different types of RMGICs, there is a difference in their water sorption characteristics (Yap, 1996; Kanchanavasita *et al.*, 1997; Toledano *et al.*, 2003). Tolendo *et al*. (2003) found that the mean water sorption of Fuji II LC was found to be (6.1 mg/mm^3 ± 1.8 SD) while Vitremer had a mean water sorption value of (7.2 mg/mm^3 ± 1.3 SD) after immersion in water for

a period of one day (Toledano *et al.*, 2003). On the other hand, Yap (1996) found that the mean water sorption value of Fuji II LC was (180.62 ± 16.23 SD) mg/ mm^3 while Vitremer was (182.11 ± 29.8 SD). Hence, water sorption is product and time dependent. Furthermore, for the same product, the evidence is conflicting due to differences in methodological parameters, duration of each study, type of resin and poly acid used and the post-curing mechanism.

Maintenance of the water balance of the GICs is a very important step that should be taken into consideration (Nicholson, 2018). One of the main functions of water are: media for setting reaction particularly during the initial setting time, solvents for dissolution of polymeric acid and water also acts as a weak Brønsted acid due to its ability to donate the proton (Kanchanavasita *et al.,* 1997; Nicholson, 2018). Furthermore, one of the main benefits of water sorption is that it counteracts the volumetric shrinkage through rapid gap reduction (Huang *et al.*, 2002; Iwami *et al.*, 1998).

The finding of this phase is consistent with Farias *et al.* (2018) who found a gradual increase in water sorption of Vitremer when immersed in acidic artificial saliva for a period of three weeks. However, when Vitremer was immersed in neutral artificial saliva, the period of water sorption lasted for two weeks which is inconsistent with the period of water sorption in the present study. However, the percentages of water uptake in the Farias *et al.* (2018) study could not be calculated for comparison with the findings of this study due to the absence of baseline values.

- **Phase II: Stationary period**

Phase II in the present study showed little change in weight percentages after the end of the 28th day of immersion, which continued until day 180. The percentages of weight change from the baseline was closer to the percentage of day 28, specifically; day 60 (5.5%), day 90 (4.9%) and day 180 (6.1%). Consequently, Vitremer's weight during these periods remained constant as shown in **Figure (5.1)** above. In this period, degradation of the fillers and matrix as well as water sorption were balanced (Iwami, *et al.,* 1998). The degradation could be linked to the continued release of the un-reacted

HEMA, Bis-GMA and other monomers which are facilitated by the softening effect due to the long period of immersion (Moszner *et al.*, 2008; Farias *et al.,* 2018). Hence, some loss of weight occurred. On the other hand, gain in weight is related to the sorption process that led to some gain. Therefore, the total net result showed no change in weight during this phase. This phase was consistent with Fano *et al.* (2004) who found that the weight of Vitremer became constant between 2 - 3 months after immersion due to the relaxation of the contraction stress (Fano *et al.*, 2004).

- **Phase III: Late slight period of weight gain**

In this phase, Vitremer showed a slight increase in weight (8.5%) in relation to the baseline. This could be linked to structural damage and fatigue of the material. Hence, water filled the spaces of the lost fillers.

The result of the present study was consistent with the long term study of Kanchanavasita *et al.* (1997) who reported an increase in the weight of the Vitremer during the application of sorption cycle tests over nine months. When Vitremer was immersed in artificial saliva, the percentage of the increase in weight of Vitremer in the first cycle was found to be (9.9% ± 0.6 SD) (Kanchanavasita *et al.*, 1997). The sorption percentage was increased to (4.8% ± 0.8 SD) in the first cycle as well. Kanchanavasita *et al.* (1997) related the findings to the presence of the un-reacted monomer or unsaturated HEMA monomer with double bond structure. With prolonged exposure to saliva, these monomers are released and the net result is loss of weight of the specimens. However, under the same condition, the same author found that Vitremer absorbed half of this amount when it was stored in distilled water during the same period (4.5% ± 0.3 SD). Kanchanavasita *et al* linked this increase to the fact that the sorption process is controlled by both diffusion and ongoing structural changes that occur in the material during the immersion period. It is important to bear in mind that the results of the first cycle of the Kanchanavasita *et al.* (1997) study are used for comparison with the present study rather than the second cycle, due to the fact that the author suggested the possibility of structural breakdown of the sample used in the second cycle.

The finding of the current investigation is consistent with Mackenzie *et al*. (2003) who found that Vitremer had 5.38% water uptake over a one year period. However, Mackenzie *et al.* (2003) did not mention the baseline weight values as well as values after one year in spite of mentioning that water sorption led to a 0.57% mass gain. They did not mention the pH of the artificial saliva either. Furthermore, although Mackenzie *et al*. (2003) had mentioned that they had done the artificial saliva formulation according to Nicholson and Wilson *et al.* (2000), they did not cite this article in the reference list to guide the reader for more information about the pH of the artificial saliva, whether it was neutral or acidic.

It is important to mention that Fano *et al.* (2004) and Emamieh *et al.* (2011) studied the water sorption of Vitremer over various time periods in order to study its long term effect. Both authors used water as a neutral media. Fano *et al.* (2004) found that there was initial swelling after 24 hours till day 21, since they examined the specimen periodically under fluorescent light in water (pH = 7). The maximum increase in weight of Vitremer was found to be around 5.03%. Thereafter, the swelling became constant until the third month. However, after that, over a longer period, Fano *et al.* (2004) found that when the swelling reached the level of no progression, the weight decreased slowly. In particular, Fano *et al*. (2004) revealed that the loss of weight was related to loss of 20 µm thickness of the surface layer. This trend was consistent with the findings of the present study in neutral saliva media, with exception to the last phase. However, the present study measured the effect in a shorter period than Franco *et al*. (2004). This could explain why the phase of reduction in the weight of Vitremer in saliva media was not apparent in the present study as shown in **Figure (5.1)**. On the other hand, Emamieh *et al.* (2011) found that the water sorption persisted throughout the study period. Emamieh *et al.* (2011) also found that the mean percentages of water sorption of Vitremer were more than 1% when measured at each time interval (7 periods of time); starting from 24 hours to one year of immersion (Emamieh *et al.*, 2011). They also found that the layered specimen absorbed more water than the bulk filled specimen without mentioning the reason for this finding. Thus, the Emamieh *et al.* (2011) findings are inconsistent with the present study findings.

In essence, although considerable data are available in the literature, it is very difficult to correlate them as shown in **Tables (5.1) and (5.2)** that represent acid and saliva respectively. This could be linked to the confusion of some authors during the interpretation of the interaction between the water sorption and loss of the material particles. Moreover, some authors were confused when defining the point of water sorption because they only considered that it meant water gain. In fact, the reality showed that water sorption is the difference between water gain and dissolution of low molecular weight molecules (Kanchanavasita *et al*., 1997). In addition, the difference in curing method, whether by means of a halogen lamp or light-Emitting Diode (LED), could affect the water sorption and hence lead to a difference in the reported results of Vitremer restorative material (Antonson *et al*., 2008). Furthermore, another reason could be related to the variety of compositions of artificial saliva which differ widely in the literature as shown in **Table (5.2)** below. Likewise, some authors did not mention the formulations or even the pH of the media such as Kanchanavasita *et al*. (1997). Some used acidic artificial saliva while others used a neutral one. Others used water as a neutral media. The closest formula to the present study was the McKenzie *et al*. (2003) artificial saliva formula. Nevertheless, McKenzie *et al*. (2003) did not mention the pH of artificial saliva nor how they adjusted it. However, McKenzie *et al.* (2003) included carbonate and nitrate in the formulation which was absent in the present study. Furthermore, they did not use calcium or phosphate that was used in the present study which are considered important elements of saliva. Hence, this variation in the literature could subsequently lead to different effects on Vitremer weight as well as its ability to absorb water.

Table (5.2): The reported studies with different formulations of artificial saliva solutions to use for measuring the water sorption and /or the weight changes of Vitremer restorative dental material.

Study	Study title	Saliva formulations	Results of the study
The present study	Comparative *in vitro* study of selective physical properties of Activa, Cention N and Vitremer	Calcium 1.5 g, Phosphorus 0.8833 g, Potassium chloride 111.825 g, 1 liter of water Full strength HCL was used to adjust the pH to be 7	Significant total weight gain (4.3%) over a period of a year in relation to the baseline. The percentage of increase in the studied periods of time as follows; day 1 (1.2%), day 2 (1.3%), day 7 (0.7%), day 14 (2.9%), day 21 (4.98%), day 28 (6.6%), day 60 (5.5%), day 90 (4.9%), day 180 (6.1%), day 365 (8.5%).
(Farias *et al.,* 2018)	Water sorption and solubility of glass ionomer cements indicated for atraumatic restorative treatment considering the time and the pH of the storage solution	Authors mentioned that they used acidic saliva and neutral saliva without mentioning any formula or pH for both of them	- Water sorption in acidic artificial saliva was increased gradually as follows during the studied four periods of time; day 1 (88.37 µm), day 2 (101.66 µm), day 14 (113.38 µm) and day 21 (114.41 µm). - In neutral artificial saliva there was initial increase in day 1 (77.76 µm), day 7 (79.67 µm), and day 14 (85.33 µm) followed by reduction in

			day 21 (79.69 µm) The baseline values were not mentioned in the article.
Emamieh, Ghasemi *et al*., 2011)	Hygroscopic expansion of Aesthetic Restorative Materials: One-Year Report	Distilled water The pH of the water was not mentioned.	Percentage of water sorption in seven periods of time was found to be more than 1% (in all of the studied seven periods of time) over a year.
(Fano *et al*., 2004)	Hydrolytic Degradation and Cracks in Resin-Modified Glass-Ionomer Cements	Neutral solution at pH = 7. The author did not mention the formulations of the neutral media	There was total weight loss from the beginning till the end of the study period. The erosion rate of the Vitremer ER=1.5* 10^{-3} per month. There was initial weight gain to maximum percentage of 5.03% on day 21. There was loss of image resolution when fluorescent dye was used after one day of immersion that confirms initial absorption of water. The baseline values were not mentioned in the article.
(Aliping-McKenzie *et al*., 2003)	The effect of saliva on the surface hardness and water sorption of glass ionomers and ‘’compomers’’	NaCl 0.5 g/L, $NaCO_3$ 4.2 g/L, $NaNO_2$ 0.03 g/L, KCl 0.2 g/L	Percentage of equilibrium water uptake over the period of one year in artificial saliva was found to be equal to 5.38%. Likewise, the percentage of increase in weight was equal to 0.57% The baseline values, pH values of the storage solutions were not mentioned.

(Toledano *et al.,* 2003)	Water sorption and solubility of resin based restorative dental materials	Distilled water. The pH of the distilled water was not mentioned.	Water gain (mean water gain of the Vitremer was 6.1 µg/mm^3 ± 1.3 SD). The baseline value was not mentioned by the author.
(Akashi *et al.,* 1999)	The relationship between the water absorption characteristics and the mechanical strength of resin-modified glass ionomer cements in long term water storage	Water. The pH of the water was not mentioned by the author.	Water uptake of Vitremer (9.2% ± 0.5 SD) to reach the equilibrium of water uptake after one year
(Cattani-Lorente *et al*., 1999)	The effect of water on the physical properties of resin-modified glass ionomer cements	Water. The pH of the water was not mentioned by the author	There was linear increase in the volume of the Vitremer by 1.1% after immersion in water for one day. There was initial increase in sorption values in day 1 (113.9 µm/cm^3), day 7 (140.6 µm/cm^3), day 15 (144.8 µm/cm^3) and day 21 (146.2 µm/cm^3) followed by reduction in day 21 (143.4 µm/cm^3). The baseline values were not mentioned in the article.

(Iwami *et al.*, 1998)	Weight change of various light-cured restorative materials after water Immersion	Water. The pH of the water was not mentioned	From the graph Vitremer has gain weight from the baseline by around 80%
(Kanchanavasita *et al*., 1997)	Water sorption characteristics of resin-modified glass ionomer cements	Artificial saliva formulation and pH were not mentioned in the article.	Weight was increased in the first cycle by (9.9 % ± 0.6 SD). The sorption percentage was also increased at the first cycle by 4.8% ± 0.8 SD).
(Nicolson, 1997)	The physics of water sorption by resin-modified glass ionomer dental cement	Vitremer was stored in • Water • 0.9% NaCl • 1 M NaCl The pH of the three solutions was not mentioned by the author.	• When Vitremer was immersed in water for ten days and cured for 30 seconds, the percentage of water uptake was found to be equal to (7.42% ± 0.3 SD). • Storage of Vitremer in salt solution led to less absorption of water. In particular, 0.9% of NaCl was found to absorb higher amount of water (7.71% ± 0.39 SD) than 1 M of NaCl (6.63% ± 0.21 SD). This was the case when Vitremer was cured for 20 seconds and immersed for ten days.

This would lead to the subsequent difference in surface reaction of Vitremer with saliva as the ionic strength will vary as shown in **Table (5.2)** above, therefore, the osmotic pressure also varied, which leads to different outcomes. Furthermore, some authors used neutral artificial saliva while others used acidic artificial saliva. This fact is in accord with the fact that natural saliva differs from one human to another and even within the same individual at different times and in different situations, depending *inter alia* on the condition of their health. Hence, the organic and inorganic solid constituents of saliva are different (Keyf & Yalcin, 2005). Consequently, the evidence is conflicting due to lack of standardization.

5.1.2. Association of Activa Bioactive Restorative weight and height changes

The findings of the present study showed that the association between the weight of Activa and time of immersion in acidic media over 10 periods of time was positive ($1.083E^{-6}$). On the other hand, the association of height for one year immersion time was found to be negative in Activa ($-1.598E^{-7}$). Generally, this means that as the weight of Activa increases, the height decreases over the period of one year. However, this association is not significant (p = 0.698) for weight or height (p = 0.971). In the first phase, there was an initial increase in weight and height for the period of one month as shown in **Figures (4.3) and (4.9)**. Increase in weight at the beginning of the experiment could be related to the water sorption. Water sorption in Activa could be related to the presence of hydrophilic-ionic resin that is found in the rubberized matrix as mentioned by the manufacturer, or to methacrylate monomers as stated by the material safety data sheet (Activa Bioactive, 2016). However, no study had been found in the literature on this topic. This initial phase is similar to the Vitremer phase. However, the slope of Activa ($1.083E^{-6}$) was found to be lower when compared to Vitremer ($1.665E^{-5}$) in spite of the fact that the trend of weight gain was similar in both materials due to the stabilization of water sorption by phosphate in Activa (Tiskaya *et al.*, 2019; Liu *et al.*, 2020) which was absent in Vitremer (Xu *et al*., 2008; Zhang *et al*., 2016). Phosphorus is considered an essential element to promote biological growth as well (Liu *et al.*, 2020). Liu *et al.* (2020) mentioned that phosphate adsorption from any material into the

solution is affected by many parameters such the pH, ionic strength and the competitive anions.

It is important to mention that the graph that represents the weight association of Activa in acid and saliva media had a similar pattern in the first phase which lasted for one month. However, in the second phase, the association of weight became positive in acid media while it was negative in saliva media. However, the weight gain in acidic media could be explained as follows:

- The first theory explains the exchange of ionic molecules through the porous fillers as confirmed by the SEM images as shown in **Figure (4.26)** of Activa in saliva media. The SEM images showed some changes in the back scattering property as the fillers became darker or absorbed light. Release of calcium molecules from the pores of fillers could allow the influx of water into the material. Calcium is released to acidic media to form calcium lactate and hence, elevate the pH. Hence, the smart behaviour of the material could be related to these porous ‘‘alkaline fillers’’. Simultaneously, the height in acidic media decreases and the surface roughness increases due to the loss of some rubberized matrix in the long term. However, this change is not statistically significant for the parameters. It is important to mention that the acidic solution used in the present study did not contain any calcium; hence, calcium is released into acidic solution in high percentages to neutralize the media.
- The other theory explains the continuous release of calcium. When calcium is released in the early days of the study, the solution is replenished during each period of time. The acidic media that is made in the lab does not contain calcium. Hence, calcium is released from Activa through the whole duration of the study, which leads to depletion or dissolution of this ion from the fillers. Depletion of ions from the Activa samples results in a change in the concentration gradient which leads to an influx of water through the porous fillers and hence an increase in total weight of the specimen. The concentration of calcium ions is higher than in saliva media. This is due to release of calcium from the ionomer type of glass filler (Ruengrungsom *et al*., 2020).

As claimed by the manufacturer, and proved by Tiskaya *et al*. (2019) calcium ions were found in high percentages in Activa. Tiskaya *et al.* (2019) proved that some ions such as calcium and silicone were released when Activa was immersed in acidic artificial saliva (pH = 4) in eight periods of time. Tiskaya *et al*. (2019) further mentioned that Activa is able to increase the pH (pH = 4) of the acidic artificial saliva media upon immersion. Moreover, Ruengrungsom *et al*. (2020) recently found in their elemental analysis that Activa contains calcium. However, this author mentioned that the release of calcium is less in Activa than in Cention N. Ruengrungsom *et al.* (2020) assumed that this could probably be related to the presence of only one type of glass filler in Activa, which is the ionomer type that only releases calcium when subjected to acidic challenge. Ruengrungsom *et al*. (2020) mentioned that this phase contains phosphate as well. Consequently, Activa contains higher amounts of phosphate than Cention N. Phosphate is an important element for stabilization of the sorption process. This could also explain why Activa has a clearer water sorption period than Cention N. Therefore, the calcium/phosphate assembly would act together to neutralize the acidic media. This interaction takes place through release of these ions to the acidic solution and the exchange of protons leads to change in the concentration gradient and hence total network increase in the weight of Activa.

Calcium ions are considered one of the network-dweller ions that works as a network modifier through the formation of Si-O-Ca^{2+} bonds and could therefore make the glass incorporation more basic (Maeyer *et al.,* 1999). Furthermore, calcium ions are highly soluble in water against the hydrophilic surfaces (Vogler, 1998). Hence, a certain level of hydrophilic behavior is considered as a prerequisite for bioactivity. However, in order to reach a conclusion regarding this information, it is logical to examine whether Vitremer has the ability to recharge calcium from the glass fillers. However, Xu *et al*. (2008) and Zhang *et al*. (2016) mentioned that Vitremer is depleted from both calcium and phosphate. Hence, it does not have the ability to release these elements. Furthermore, no evidence was found in the literature to confirm whether Vitremer has the ability to recharge the external calcium. Hence, further research is needed.

On the other hand, the findings of the present study showed that when Activa is immersed into artificial saliva, the association with weight changes over a period of one year is negative, but is not significant (p = 0.998). The same applied to the height in artificial saliva as well (p = 0.928). As depicted from the graph, the initial phase of increase in height and weight is justified by water sorption for the same reason mentioned earlier for acidic media. Furthermore, the manufacturer claims that phosphate and hydroxide are in the backbone as illustrated in **Figure (2.4)** (Activa Bioactive, 2016). Hence, water sorption could be explained by the action of the hydrogen bond in water that forms due the presence of the functional hydroxyl group (-OH) which attracts water to the polymer network (Vogler, 1998; Par *et al*., 2019). Hence, the properties of the solvent could control the biological response of this material (Vogler, 1998; Par *et al*., 2019).

However, as the specimens become aged in saliva, the material loses weight. The loss of weight could be described by the following theories:

- Loss of weight in saliva media after one year is only related to the loss of the rubberized matrix that contains UDMA and hydrophilic methacrylate based monomers as stated by the FDA report. This is confirmed by the Ra graph which showed an increase in Ra. In this phase, there is also no major exchange in calcium ions due to its presence in artificial saliva. Ruengrungsom *et al*. (2020) mentioned that in a neutral condition, the ionic glass particles do not release calcium; hence, there is no major exchange of this ion with artificial saliva media.
- Loss of weight could be explained by the balance in different cycles of calcium, or phosphate release and re-release. The first cycle started with calcium release during the sorption process when artificial saliva was changed frequently during each period of time and calcium recharge from artificial saliva took place through the porous fillers. This explanation was confirmed by SEM after one year which showed that the post-experimental image had the same backscattering as the pre-experimental image.

The finding of the present study is inconsistent with Porenczuk *et al*. (2019) who studied the effect of the release of fluoride on the weight of Activa. The author found a loss of

weight of Activa of 76% from the baseline for the period of two weeks. However, this author immersed Activa in de-ionized water. The author stated that this loss was due to the loss of ions, including fluoride that showed a burst effect in the first week, as well as silicone release due to breakage of Si-O-Si bonds (i.e.15.5 ppm was released on the first day, followed by some decline to 3 ppm while continuously forming a plateau until the end of the study). Furthermore, Porenczuk *et al*. (2019) suggested that the compositions of the bioactive glass has a major influence on the release of fluoride. However, this point still needs appraisal due to the lack of specific knowledge about the exact composition of Activa. Furthermore, their methodology was different as they aimed to measure the fluoride release. In addition, the author did not specify in the methodology whether they measured height and thickness following certain guidelines or standards. Moreover, the release of fluoride, especially on the first day, could be high due to the fact that they used phosphoric acid in the experiment which is a very strong acid. Porenczuk *et al*. (2019) used a LED diode polymerization lamp which is the same type of Elipar curing unit used in the present study. However, the intensity of Radii plus (1500 mW/cm^2) differs from Elipar light curing (1200 W/cm^2). Hence, the degree of conversion could be different.

5.1.3. Association of Cention N weight and height changes

The findings of the present study showed a non-significant negative association between the weight of Cention N when immersed in acidic media over a one year period (p = 0.957). The same finding applied to the height (p = 0.626). This association of weight loss in Cention N was the least among the three materials from the baseline. The slope of weight was negative by (-1.15E^{-6}) which is less than the slope of Vitremer (-8.0022E^{-5}) and Activa (-4.494E^{-6}) per unit of time. This negative association was also reported when Cention N was immersed in saliva for a period of one year (-1.9465E $^{-6}$) and it was insignificant as well (p = 0.948). This negative association was also found in the height for artificial saliva (p = 0.621). However, this association was more negative in acidic media which could be related to the presence of some hydrophobic components that inhibit the water sorption. In particular, repulsion of water could be related to the presence of a urethane group from a hydrophobic monomer's partially aromatic urethane di-methacrylate (TMX-UDMA) that was added to Cention N to reduce

the discoloration as shown in **Figure (5.2)**. This urethane group has a major role in the formation of an intermolecular hydrogen bond, which leads to a rise in monomer viscosity and an increase in the power of repulsion (Moszner *et al.*, 2008).

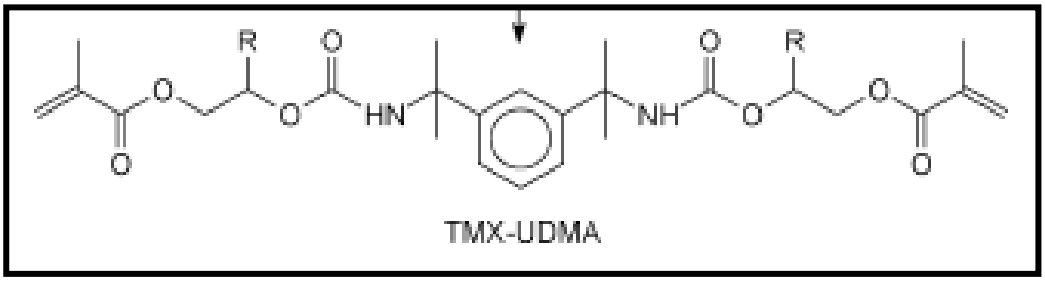


Figure (5.2): The presence of partially aromatic urethane di-methacrylate TMX-UDMA could be linked to the absence of the initial swelling (Moszner *et al.*, 2008).

The long term loss of weight could be explained by the following:

- Long term exposure to lactic acid or artificial saliva led to loss of some elements from the matrix such as barium glass; hydrophobic UDMA monomer (Müller *et al.,* 2017). Furthermore, loss of fillers was also reported (Roulet *et al*., 2020). However, this reduction in weight was not significant in both acid and saliva media which could be related to the surface treatment of the fillers. The manufacturer had mentioned that the fillers receive surface treatment (Todd, 2016). Although this treatment could be responsible for good integration between the matrix and fillers, no single study has been established in the literature about such a topic and further research is needed. Nevertheless, in the present study this finding is confirmed by the SEM image that showed minimal matrix degradation around the filler particles as shown in the post-experimental image of Cention N in acidic media and confirmed by Roulet *et al.* (2020) as well.
- Loss of weight could be linked to the release and re-release of ions from Cention N porous fillers as well (Roulet *et al*., 2020; Ruengrungsom *et al*., 2020). This could be explained for acidic media by the fact that lactic acid (*p*Ka = 3.86) displaced the polyacrylic acid (*p*Ka = 6), hence lactic acid attacked the glass core (Ruengrungsom *et al*., 2020). Consequently, this would lead to leaching of calcium and formation of soluble calcium lactate. Furthermore, it was found that

calcium is released in acidic conditions in higher percentages than in neutral conditions (Ruengrungsom *et al*., 2020). The reason could be related to the fact that the acidic conditions stimulated the release of calcium from both types of glass Cention N fillers; BAG-like calcium fluoro-silicate glass fillers (free from phosphate) and ionomer like calcium-alumino-fluorosilicate fillers that contain phosphate (Ruengrungsom *et al*., 2020). It is important to mention that the ionomer phase only releases ions when exposed to acid and enhances the breakage of the Al-O-Si bond (Ruengrungsom *et al*., 2020). These findings are confirmed in the present study by post-experimental SEM images and are consistent with Ruengrungsom *et al.* (2020) findings. Cention N released calcium as mentioned by Tiskaya *et al.* (2019) and this was confirmed by Ruengrungsom *et al*. (2020) in their elemental analysis. Furthermore, Cention N has the ability to release and re-release phosphate (Ruengrungsom *et al*., 2020). Cention N was found to release phosphate in higher quantities than Activa (Ruengrungsom *et al*., 2020).

The findings of this study are consistent with Nayak & Shenoy (2019) who found that Cention N had lesser absorption when compared to conventional GICs when immersed for one week in many different solutions, one of them was artificial saliva. However, this study was the only study that was reported about Cention N. The author used a very small sample size (n = 5) for each material. In addition, they measured the weight to only one decimal which is inaccurate for determination of weight for such a small sample. Furthermore, they did not give any information about the curing method or which curing light they used. The curing method could clearly confound the results. Furthermore, they desiccated the sample and this would make the sample vulnerable to cracking and hence deterioration of its mechanical properties before starting the experiment.

5.1.4. Comparison of the weight and height between the three restorative materials

The findings of the present study showed that when the Kruskal-Wallis test was used for comparison of the weight in acidic media between the three materials, the results were

significant for the 10 periods of time (p = 0.000) at each point of time. There was a significant difference between the groups of the studied materials until the end of the second month. When the difference in weight was measured in relation to day 0, Cention N recorded the highest weight followed by Vitremer and thereafter Activa. It is possible that Cention N recorded the highest actual baseline weight values among the three materials since the beginning of the experiment. However, in the following three periods of time Cention N still ranked the highest until the end of the experiment. Hence, it showed resistance to change in weight when compared to Vitremer restorative material. It is important to mention that this difference is a result of integration of several factors; difference in sorption characteristics of each material, the speed of degradation as well as the speed of release of un- reacted monomers (chemical compositions), proportion of the resin in the cement and difference in degree of polymerization (Kanchanavasita *et al.,* 1997; Iwami, *et al,* 1998; Cattani-Lorente, *et al*., 1999; Müller *et al.,* 2017).

In fact, Cention N could be more resistant to the effect of degradation by lactic acid. Furthermore, the components of Cention N, such as nature of the polymer backbone and the degree of hydrophilicity are all important in weight change determination (Gajewski *et al.*, 2012). This is probably related to the fact that the water sorption capability of the material is more or less related to the degree of conversion, filler contents, matrix polarity, and topography of the polymer chain and particle size of each material (Müller *et al.,* 2017; Farias *et al.,* 2018). One of the components of Vitremer is Bis-GMA which showed a lower degree of conversion when compared to the TMX-UDMA, UDMA monomers of Cention N (Moszner *et al.*, 2008; Gajewski *et al.*, 2012). In particular, the higher intrinsic reactivity of Cention N could probably be due to the presence of the hydroxyl group in their chemical backbone as well as pi-stacking (π-π) interactions in the aromatic ring. Therefore, the highly reactive compounds in Cention N could lead to a higher degree of resistance to chemical degradation. Consequently, the amount of un-reacted monomer released from Cention N upon immersion would be lower. For that reason Cention N would have higher weight than Vitremer. Moreover, in addition to the presence of the hydrophilic HEMA monomer in Vitremer, TEGDMA, with a low molecular weight, is a highly flexible component that was added to the Bis-GMA in

the Vitremer structure to increase water sorption. It also affects the color stability as seen in the stereo-microscopic image **(Figure 4.25).**

For the *following three periods* of time in this study, when the materials aged in the lactic acid, changes in weight between Vitremer and Activa became insignificant. This could be related to the fact that the wear rate of the Vitremer is higher than Activa resulting in faster weight loss. Other factors could be related to the size of the dislodged particles. Loss of large size particles leads to more rapid weight loss than loss of small particles. Vitremer has very large particles when compared to Activa and Cention N as confirmed by the SEM of Vitremer and Activa in **Figures (4.25) and (4.26)** of the present study. Furthermore, Müller *et al.* (2017) mentioned that higher filler percentages led to absorption of a smaller amount of water which was justified by the manufacturer's instructions as shown for Cention N. Müller *et al.* (2017) stated that higher filler percentages would lead to less swelling of the material especially in the first days.

On the other hand, when comparison of the weight was done for the three materials in artificial saliva media, the results showed significant differences in weight between the three materials over each period of time during the study period as also seen in acidic media (p = 0.000). Following the same ranking in acidic media in relation to the baseline, Cention N was reported to be significantly higher in terms of weight when compared to Vitremer and Activa as shown in **Figure (4.18)** based on the statistical main rank of the data. Furthermore, Vitremer was reported to be significantly higher than Activa. This could be due to the same reason mentioned above. However, in the long term, as the materials aged in the saliva media on day 365, the difference in weight between Cention N and Vitremer became insignificant. This could be related to the effect of the reacted and un-reacted HEMA monomer in Vitremer: the reacted part that is found in the monomer attracts water, while the un-reacted part is released as Vitremer aged; hence, water occupied the spaces to facilitate weight gain. Furthermore, another effect is the effect of the siloxane group mentioned by Mulder & Anderson-Small (2019). The siloxane group of the glass filler particles dissociates into a silanol group (-Si-OH) (Czarnecka *et al*., 2015). This group is more hydrophilic and leads to an increase in the amount of the absorbed water with consequent increase in weight

(Mulder & Anderson-Small, 2019). This fact is applied to Vitremer as well. On the other hand, Cention N has hydrophobic monomers that repulse water as mentioned above.

In conclusion, the trend of weight changes over one year for each studied material differs. This could be explained by the difference in the compositions, their water sorption abilities, monomers and ions incorporated, as well as the ratio of the resins to salts in the material matrix. When talking about the percentage of the resin and taking Vitremer as an example, Vitremer has a high resin content according to the manufacturer (Yap, 1997). As stated by Yap (1997), an increase in the percentage of resin would lead to an increase in the amount of water sorption. Hence, the amount of water sorption could be a clear representation of the resin component in the RMGICs (Yap, 1996; Kanchanavasita *et al.,* 1997). In addition, the more salts engaged in the material matrix such as in Vitremer, the more sensitive to changes in pH are materials that have a predominant resin matrix. Furthermore, the weight changes that occur in the three materials could be confounded by the fluoride release that could not be investigated in the current study. The release of fluoride in the immersed solution usually took place in two ways; either through diffusion within the material or dissolution at the surface (Al-Naimi *et al.,* 2008). However, both of these mechanisms usually lead to total weight loss of the material and should be considered when interpreting the association between the weight and height of the three materials.

5.2. Association of surface roughness changes over a one year duration (going through ten periods of time)

It is important to mention that all the materials tested showed a positive association when immersed in acidic or saliva media. However, some materials do not show any statistical significance to an increase in Ra values. The increase discussed in this chapter is based on many parameters that affect the surface roughness of the restoration such as; the composition, filler size, filler load and the degree of conversion (Amaechi & Higham, 2005; Hamouda, 2011). Furthermore, interfacial bonding strength, porosity, percentage of the cured material and the degree of polymerization as shown in **Figure (5.3)** below are also factors that may affect the surface roughness (Borges *et al.,*

2011; Briso *et al.,* 2011; Paula *et al*., 2011; Pacifici *et al*., 2013; Beresescu *et al.,* 2015; Rodrigues *et al*., 2015).

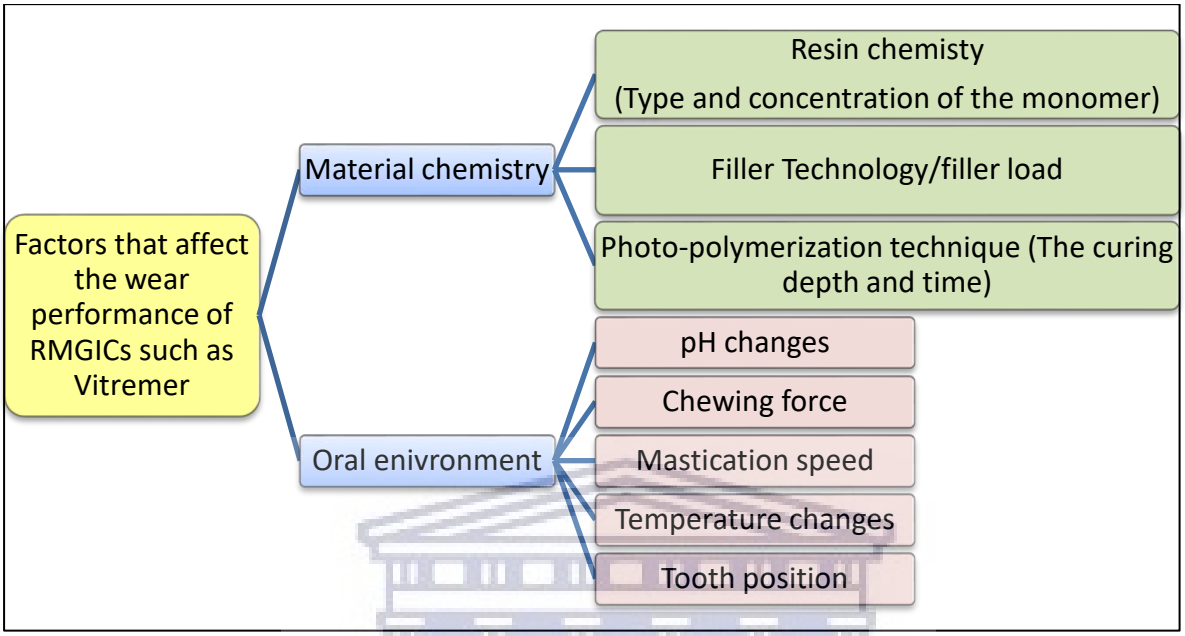


Figure (5.3): Factors that affect the wear of tooth colored restorations (Borges *et al.,* 2011; Briso *et al.*, 2011; Rodrigues *et al*., 2015; Osorio *et al.,* 2016; Kumar *et al*., 2020).

Wear resistance is a very important property in selecting any restorative material that is safe for clinical use (Yip *et al.*, 2004; Honório *et al.*, 2008; Momesso *et al*., 2010; Briso *et al.*, 2011; Hamouda, 2011; Erdemir *et al.,* 2013; Kazak *et al.,* 2020). The fundamental purpose of doing any restorative procedure is to obtain smooth surfaces on the restoration without any internal or external surface porosity (Hamouda, 2011). The literature describes the concept of dental wear as an outcome of interactions between two moving surfaces, which results in a gradual removal of the material (Beresescu *et al.,* 2015). There are two fundamental reasons for the dental wear of any restorative material: *1) Mechanical wear:* This is usually referred to in the literature as abrasion of the restorative material (Carvalho *et al*., 2008), *2) Chemical wear:* Usually known in the literature as erosion of the dental material (Nicholson *et al.*, 1999). In the clinical setting, when acidic beverages are consumed, the two types of dental wear occur together due to the fact that abrasion occurs during mastication as well (Beresescu *et al.,* 2015;

Kumar *et al*., 2020). In addition, the location of the clinical wear could be in the occlusal free area or contact free area (Mazumdar & Chowdhury, 2018).

It is important to mention that consumption of acidic drinks is continuously increasing among child populations (Honório *et al.*, 2008; Kumar *et al*., 2020). Vitremer, like any restorative material, is vulnerable to destruction by continuous or intermittent attacks of chemically degrading acidic beverages, alcohol, toxins from plaque, enzymes or consumption of fruits (Hamouda, 2011; Correr *et al.,* 2012; Rodrigues *et al*., 2015). Bollenl and Lambrechts *et al*. (1997) found that the threshold of the surface roughness (Ra) value of any restoration is around 0.2 µm. Thus, if the Ra value exceeds this number, plaque biofilm will accumulate (Bollenl *et al.,* 1997). It is important to mention that dental wear of Vitremer is affected by two factors; patient factors and restoration factors. Regarding patient factors, wear changes are related to consumption of acidic drinks and are influenced by external or internal parameters (Amaechi & Higham, 2005). The external parameters are as follows: the frequency of intake of acidic drinks, the duration of time in which these drinks last in the mouth, the temperature, pH of the acidic drinks, method of drinking whether a cup or straw, oral hygiene practices and also chronic intake of acidic medicaments (Amaechi & Higham, 2005; Pacifici *et al*., 2013; Beresescu *et al.,* 2015; Rodrigues *et al*., 2015; Kazak *et al.,* 2020; Kumar *et al*., 2020).

Furthermore, internal factors could also play a role, such as the presence of medical factors such as, bulimia nervosa or gastro esophageal reflux disease (GORD), changes in salivary amount (consistency that could vary from patient to patient, the flow rate which could also change even for the same patient from time to time) (Amaechi & Higham, 2005). In laboratory studies, the type of storage media, such as water, acidic media (Correr *et al*., 2012) and artificial saliva (Honorio *et al*., 2008) could also affect the wear of Vitremer.

The clinical effect of the increase in wear values is noticed by a change in the optical properties or surface discoloration and hence the aesthetics, attachment of plaque micro-organisms on the restoration and reduction in the mechanical properties and therefore, final fatigue of the restorative material (Momesso *et al*., 2010; Hamouda,

2011; Erdemir *et al.,* 2013; Osorio *et al.,* 2016). Other factors that are more or less related to surface roughness, such as powder liquid ratio, temperature, humidity and method of curing were standardized during this study.

5.2.1. Association of Vitremer surface roughness changes

The findings of the present study showed that when *Vitremer had been immersed in acidic media,* there was a significant positive association in the surface roughness after one year of immersion (p = 0.001). The increase during the first days in the surface roughness as depicted in **Figure (5.4)** below could be explained by the interactions between the compositions and the establishment of the eroding effect of the lactic and acetic acid (Fucio *et al.,* 2008; Carvalho *et al.*, 2012).

Changes in Ra of Vitremer over a one year period could be divided into three phases: The phases are illustrated in **Figure (5.4)** below.

- Phase I: Rapid increase in Ra in early days.
- Phase II: Slow increase in Ra toward the peak.
- Phase III: Period of reduction in Ra values.

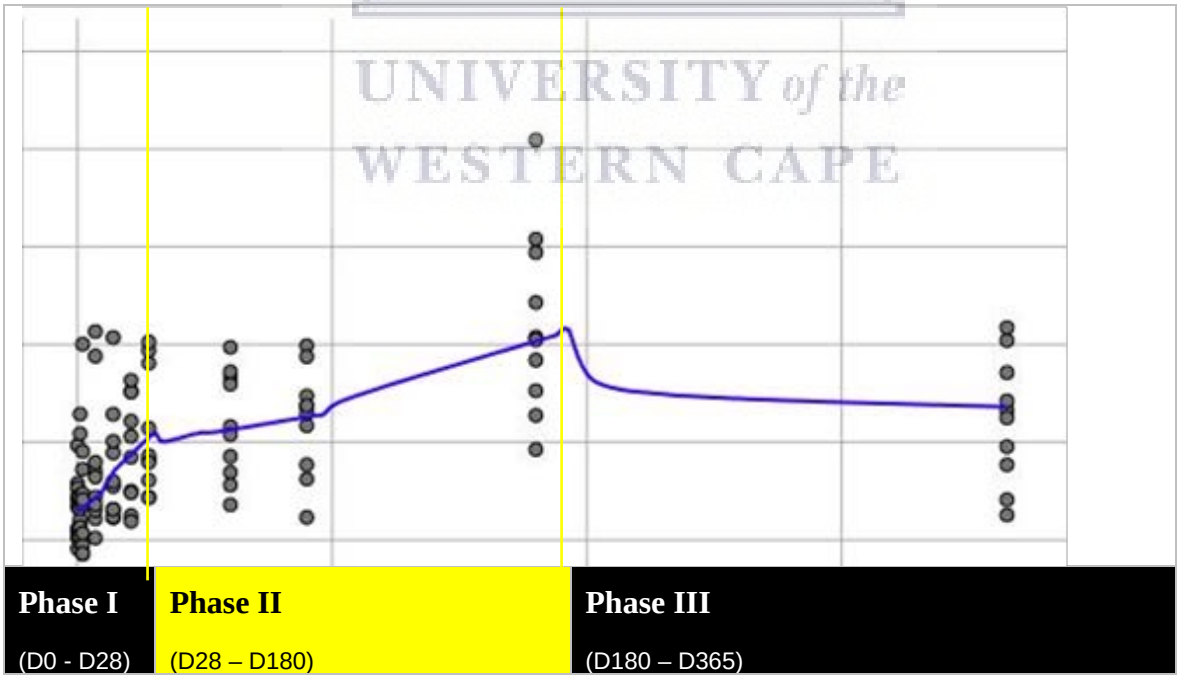


Figure (5.4): The phases of change in Ra of Vitremer in acidic media over a year.

- ***Phase I: Rapid increase in Ra***

There was a steep increase in Ra roughness in the first month. The mean percentages of increase in Ra over the first month were found to be as follows: day 1 (4.3%), day 2 (5.3%), day 7 (29.1%), day 14 (3.8%), day 21 (15.3%), day 28 (10.6%). This early phase could be explained by disintegration of the matrix which runs in parallel with the water sorption period to lead to softening of the matrix. Water could diffuse to the interface between fillers and pores to produce disintegration of the surface layer (Toledano *et al.*, 2003; Borges *et al.,* 2011; Carvalho *et al.*, 2012). Furthermore, the degradation of the matrix is enhanced by the lower degree of conversion of Vitremer, loss of some ions and low pH of the media. Toledano *et al*. (2003) and Paula *et al*. (2014) mentioned that this disintegration is related to the formation of silica at the periphery, due to the acid base reaction that took place during the early days of immersion, hence, hydrogel formation has a direct effect on Ra changes. Therefore, the fillers are still participating in the setting reaction during this maturation phase (Toledano *et al.*, 2003). The lower degree of conversion means the monomer will stay un-linked and then be released during immersion (Kim *et al.,* 2015; Müller *et al.,* 2017). Many authors rationalize the increase in Ra in the first week to the release of high percentages of an organic hydrophilic HEMA component (Fucio *et al,* 2008; Borges *et al.,* 2011; Carvalho *et al.*, 2012; Kim *et al.,* 2015). The release of other monomers such as, TEGDMA, PMMA (Poly-methyl methacrylate) and bis-GMA is also reported (Borges *et al.,* 2011). It has been mentioned in the literature and by manufacturers that the presence of a third cure reaction could have a more positive effect on the wear resistance of the material clinically (3M ESPE, 2012; Kim *et al.,* 2015). However, the degree of conversion in Vitremer is related to two factors; the depth of cure and presence of the monomers (Palmer *et al.,* 1999; Kim *et al.,* 2015). The depth of cure factor is not relevant to the present study because the sample used was only 1 mm in thickness. Therefore, the disintegration in the present study occurred because the material sets further through the continuation of the acid base reaction over time and the presence of the HEMA monomer *per se* could result in the reduction of the speed of the acid base reaction (Palmer *et al.,* 1999; Kim *et al.,* 2015).

Furthermore, other factors that could explain the increase in the Ra of the Vitremer in the early days of immersion are the release of ions such as sodium, silica, fluoride and aluminum which act as a synergistic factor in this initial degradation and consequent weight loss. However, De Witte *et al.* (2003) revealed that the concentration of these ions in the storage solution could be a confounding factor that could affect the final surface roughness results of the present study (De Witte *et al.,* 2003). This could be related to ions such as fluoride, which is a negatively charged ion that could compete with the carboxylic group in the liquid of Vitremer to form water soluble compounds with the positively charged aluminum. Hence, all of these factors could explain the higher Ra values during the early days of immersion. However, the present study is not able to ascertain the point of ion release because fluoride could not be measured in the lab.

Some authors such as Carvalho *et al*. (2012) relate the increase in the Ra of Vitremer to the release of fillers. There are two contributing factors that enhance the release of fillers: filler size and shape. Vitremer has large filler particles. The average particle size of the Vitremer is around (3 µm) (Carvalho *et al.*, 2012; Paula *et al*., 2014; Osorio *et al.,* 2016). It is noted in the literature that the larger particle size is usually difficult to finish and polish and usually results in higher roughness values at the beginning of the experiment (Erdemir *et al.,* 2013). This could be explained by the fact that the larger the particles, the lesser the packing and cohesion and hence it is more susceptible to degradation than the smaller size particles. Furthermore, Vitremer has irregular filler shapes which makes ''the pluck out'' of the fillers from the resin matrix easier (Carvalho *et al.*, 2012). Moreover, the glass component in the powder is less homogenous and hence could provide a rougher surface (Briso *et al.,* 2011).

The finding of the current investigation is consistent with Hamouda (2011) who found a significant increase in the mean Ra of Vitremer samples when the materials were immersed in Mirinda and mango juice. Both juices had low pH; (2.85) and (3.49) respectively as shown in **Table (5.3)** below. However, the duration of Hamouda's study was limited to one week which is shorter than the period of the current study. Furthermore, the baseline values were not documented by the author. Moreover, the chemical formulations of Mirinda and mango juice used in the Hamouda study were not

described. In addition, they measured the Ra in three different directions in contrast to this study that measured it in eight different directions.

Likewise, Fúcio, *et al.* (2008) found a significant change in the surface roughness when Vitremer was placed in an acidic bacterial bio-film in the agar plate (around 1.109 µm). However, the study was conducted for a short period, one month in particular (Fúcio, *et al.,* 2008). Furthermore, Fucio *et al.* (2008) used a different methodology and some information was not mentioned, such as the pH of the streptococcus biofilm, the concentration and type of the acid produced.

In addition, the result of the current research is consistent with Carvalho *et al*. (2012) who found that Vitremer showed a significant increase in the percentage of Ra by 420% (more than four-fold) from the baseline value when pH cycling in combination with mechanical brushing was applied to Vitremer for 10 days with a cycling duration of 6 hours/day. However, if Vitremer was only subjected to pH cycling, the percentage increase in Ra was found to be around 15% which is insignificant when compared to the baseline. The interaction between the re-mineralizing and de-mineralizing solution could reduce the acidic effect on the surface of Vitremer when compared to the current investigation, in which the acid was used for the whole duration without placing the specimens in a re-mineralizing solution. Furthermore, another difference between the Carvalho *et al.* (2012) findings and the findings of the current investigation is the application of additional intervention (brushing). In this study, only chemical intervention was applied.

Moreover, Briso *et al.* (2011) found similar results and stated that there was a significant increase in the Ra of Vitremer when immersed in Sprite (124%) and hydrochloric acid (6.3%) for a period of five weeks. The authors mentioned that the increase could be related to the matrix dissolution as well as the elution of a number of fillers. Briso *et al.* (2012) also considered that the eluted particles from Vitremer could have a buffering effect on the acidic media. However, there are some differences between the Briso *et al.* (2011) findings and the findings of the present study; phosphoric etching of the surface of the Vitremer specimens was done before immersion into Sprite/hydrochloric acid.

Similar findings were recorded by Paula *et al.* (2014) who found a significant increase in the mean Ra percentages of Vitremer after immersion in orange juice (44.1%) and Cola drink (23%) for a period of one month. Paula *et al.* (2014) rationalized this to the presence of phosphoric acid in the Cola drink as well as citric acid in orange juice. Furthermore, the author mentioned that the reason for the increase in Ra is related to the release of HEMA and TEGDMA from the matrix. However, the duration of the study by Paula *et al*. (2014) was limited to one month which is shorter than the period of the present study.

- ***Phase II: Slow increase in Ra toward the peak***

After completion of the steep increase phase in Ra values, the second plateau phase showed an increase in mean percentages of Ra values as follows: day 60 (13%), day 90 (7.2%) and the peak was found to be in day 180 (56.5%). In this phase, the polymer started aging in the acidic solution. The increase in Ra could be explained by the degradation of particles and initial micro-morphological damage due to the continuous penetration of acid. Cracks were also noticed on the surface on the sixth month. The presence of cracks after prolonged immersion in acidic media is consistent with Fano *et al.* (2004) who explained that the presence of cracks when Vitremer was immersed in lactic acid (pH = 3.5) was due to relaxation of the contraction stress by water absorption for a prolonged period. Consequently, microcracks are formed in day 150 within the matrix or resin filler interface resulting in cohesive or adhesive failure (Fano *et al*., 2004). Fano *et al*. (2004) mentioned that contraction stress usually requires a long term follow up study in order to be detected in the specimens. This is consistent with the current research where cracks only started to appear after six months. However, the Fano *et al.* (2004) study period was longer than the present study (around 20 months). Furthermore, Fano *et al.* (2004) used light fluorescence to detect the changes.

The finding of the present study is inconsistent with Correr *et al*. (2012) who found an insignificant change in the Ra of Vitremer after 6 months of immersion in lactic acid. Correr *et al.* (2012) evaluated the Ra of Vitremer for different periods of time for duration of 6 months after immersion in many different acidic solutions; lactic acid, citric acid, Cola drink. This author measured the Ra of Vitremer at four periods of time after

immersion; day 7, day 30, day 90 and day 180. With lactic acid, Correr *et al*. (2012) found an initial reduction in the Ra of Vitremer by (8.3%) on day 7, followed by an increase in the Ra at the following periods of time which was not statistically significant from the baseline; day 30 (8.3%), day 90 (64%) and day 180 (58%). The Correr *et al.* (2012) findings are inconsistent with the findings of the current study as the pH of the lactic and citric acid used is equal to 5.5 which is the borderline value for de-mineralization. The pH of the lactic acid used in this study is equal to 3 which could have a more erosive effect on Vitremer specimens, although Correr *et al*. (2012) used the same concentration of lactic acid as was used in the present study (0.1 mol/L). However, the main similarity between Correr *et al.* (2012) and the present study is the discoloration of the Vitremer samples.

- ***Phase III: Period of reduction in Ra values***

On day 365, there was a reduction in the Ra values by (24.3%) from the baseline. This period could be related to further damage to the peak indentations of the material that led to the formation of a slightly smooth surface, in addition to the fact that acid erodes both the filler particles and the matrix, as clearly depicted in the SEM for acid media in **Figure (4.25)**. The finding of the present study is inconsistent with De Gee *et al*. (1996) who found that the wear rate of Vitremer after a year was higher in neutral conditions (96 µm/200000 cycle) when compared to acidic condition (pH = 5) at the same time period (85 µm/200000 cycle). Yet, De Gee *et al.* (1996) found a reduction in the Ra of Vitremer when it was subjected to acid (at 15% slip) for a period of one year, which is consistent with this phase. The author explained that the cracks present were due to permanent deformation of the matrix on the Vitremer surface and were usually worn off from the outer surface irregularly. Hence, this led to a reduction in Ra values. In particular, De Gee *et al*. (1996) measured Ra values in neutral media at four periods of time and reported a gradual reduction in Ra after a year as shown in **Table (5.3)** below. This finding contradicts the finding of the current investigation. However, De Gee *et al*. (1996) did not mention the baseline value which renders comparison with the findings of the present study inaccurate. Furthermore, the author covered the specimens with finishing gloss which was not applied in the current investigation. Furthermore, the

author did not mention the formulations of neutral and acidic media. Evidence is lacking particularly for the long term effect of acid on the Vitremer surface.

The SEM images of Vitremer in acid media in the present study were consistent with Paula *et al*. (2014) who mentioned that the change in the Ra of Vitremer was related to the dissolution of silica hydrogel around the glass particles. Hence, this has a big influence on the Ra changes of Vitremer. However, this explanation could be applied to the Paula *et al*. (2004) study because they conducted their study for one month. In the present study, the crack formation is mainly the reason for the increase in Ra values in relation to baseline as the SEM was taken after a year. Furthermore, Paula *et al*. (2014) took the images on a higher magnification level (3000 X) than the highest level of magnification used in the present study.

In conclusion, the evidence is conflicting and difficult to compare when considering the effect of acidic challenge on the Ra of Vitremer. These conflicting outcomes could be related to differences in concentrations, types of acid, the pH of acidic media and the duration of each study. This variation is clear in the **Table (5.3) below**. **Table (5.3)** also clearly shows that Correr *et al*. (2012) used the same concentration of lactic acid as was used in the present study. However, Correr *et al*. (2012) used a higher pH level. On the other hand, Paula *et al*. (2014) and Hamouda (2011) used a pH level closer to the pH used in the present study.

Table (5.3): Shows the reported studies with different formulations of acidic media solutions that were used to measure Ra of Vitremer restorative dental material.

Author	Study title	Acid formulation	pH of the acidic media	Results
The present study	Comparative *in vitro study* of selective physical properties of Activa, Cention N and Vitremer	0.1 mol/L of mixture of lactic acid and sodium lactate	2.74	Significant increase in the mean percentage (12.1%) of Ra from the baseline. The percentage of increase in Ra during the following period of time was found to be; day 1 (4.3%), day 2 (5.3%), day 7 (29.1%), day 14 (3.8%), day 21 (15.3%), day 28 (10.6%), day 60 (13%), day 90 (7.2%), day 180 (56.5%). However, on day 365 there was a reduction in the Ra values by (24.3%) from the baseline.
Paula *et al*.,2014)	Influence of Chemical Degradation on the Surface Properties of Nano Restorative	• Coca-cola: carbonated water, sugar, caffeine, caramel color, natural flavour, and	• Cola = 2.49 • Orange juice = 3.23	There was a significant increase in the mean percentage of Ra after Immersion in Coca-cola (23%) and orange juice (44.1%) from the baseline value for a period of one month.

	Materials	phosphoric acid. • Orange juice: water, sugar, orange juice, natural flavour, citric acid, ascorbic acid and antioxidant.		
Carvalho *et al*., 2012)	Effect of Chemical and Mechanical Degradation on Surface Roughness of Three Glass Ionomers and a Nanofilled Resin Composite	pH cycling through the de-mineralization and re-mineralization solution. The de-mineralization solution; (2.0 mM calcium, 2.0 mM phosphate), added to buffer solution of 74.0 mM acetate in pH= 4.3. The re-	4.3 For demineralizing solution and 7 for remineralizing solution.	There was significant increase in percentage of Ra by 420% from the baseline. However, when Vitremer samples were only subjected to pH cycling the Ra increased only by 15% from the baseline which is insignificant.

		mineralization solution; (1.5 mM calcium, 0.9 mM phosphate) added to a buffer solution that consisted of 0.1 mM Tris hydroxymethyl-aminomethane pH = 7.		
(Correr *et al*., 2012)	*In vitro* long-term degradation of aesthetic restorative materials in food-simulating media	• 0.1 M of lactic acid. • 0.1 M of citric acid.	pH = 5.5 for lactic and citric acid.	No significant increase in the percentage of Ra from the baseline (58%) when Vitremer was immersed in lactic acid for a period of 6 months.
(Briso *et al.,* 2011)	*In vitro* Evaluation of	Vitremer was immersed into two	• pH of HCL=1.6.	There was a significant increase in the mean percentage of Ra when Vitremer was immersed in

	Surface Roughness and Microhardness of Restorative Materials Submitted to Erosive Challenges	acidic media: • 0.01 M of HCL. • Sprite soft drink.	• pH of Sprite soft drink HCL=3.6.	Sprite (124%) and HCL (6.3%) from the baseline for a period of five weeks.
(Hamoda., 2011)	Effects of Various Beverages on Hardness, Roughness, and Solubility of Aesthetic Restorative Materials	Vitremer was immersed in the following solutions • Mirinda orange. • Natural mango juice. • Natural milk (cow milk without any powder.	• Mirinda orange (2.85) • Natural mango juice (3.49). • Natural milk (6.34). • De-	There was significant increase in the mean Ra values of sample that was immersed in Mirinda (3 ± 0.3 SD) µm and mango juice (0.3 ± 0.04 SD) µm in relation to their respective control in de-ionized water (0.1 ± 0.003 SD) µm. However, the sample that was immersed in natural milk (0.3 ± 0.004 SD) µm does not show any significant difference with respect to control in de-ionized water after one week of immersion.

		• De-ionized water as a control media. .	ionized water (6.98).	
(Fucio *et al*., 2008)	The influence of 30-day-old Streptococcus mutans biofilm on the surface of aesthetic restorative materials—An *in vitro* study	Acid that is produced by the streptococcus biofilm.	The pH, concentration and type of acid were not mentioned by the author.	Significant increase in mean Ra of Vitremer (1.9 ± 0.532 SD) after placement in acid for one months.
(Honorio *et al*., 2008)	Effect of prolonged erosive pH cycling on different restorative materials	Cola drink	pH of the Cola drink was not mentioned by the author.	Ra was significantly increased to the mean percentage of (0.5% ± 0.05 SD).

(Fano *et al*., 2004)	Hydrolytic Degradation and Cracks in Resin-Modified Glass-Ionomer Cements	Lactic acid was added to double distilled water	3.5	Qualitative result from the surface showed increase in surface texture through formation of Cracks and bubbles in the surface of Vitremer after 150 days of immersion. Crack started at the surface fillers or at bubbles.
(De Gee *et al.*, 1996)	Early and long term wear of conventional and resin-modified glass ionomers	Nature of the three solutions used in the study was not mentioned.	pH = 5, pH = 6, pH = 7	• at pH= 7 Reduction in Ra (in µm/200000 cycle) over four periods of time; 8 hours (211), day 7 (135), day 14 (118), after four months (90) and 365 days (82). • At pH = 5, Ra after 365 days was (96)

.

On the other hand, when *Vitremer was immersed in saliva media* the positive association in the surface roughness after one year was found to be insignificant (p = 0.676). As shown in **Figure (5.5)** this increase in the Ra could be related to the wash of the matrix in a cyclic pattern. Therefore, the fillers will protrude to the surface providing a rougher surface. This is clearly depicted in the scanning electron microscopy in **Figure (4.25)** which shows that the filler is pronounced due to the degradation of the matrix and subsequent release of the monomers. Hence, the mechanism of interaction of Vitremer with saliva is different from acid.

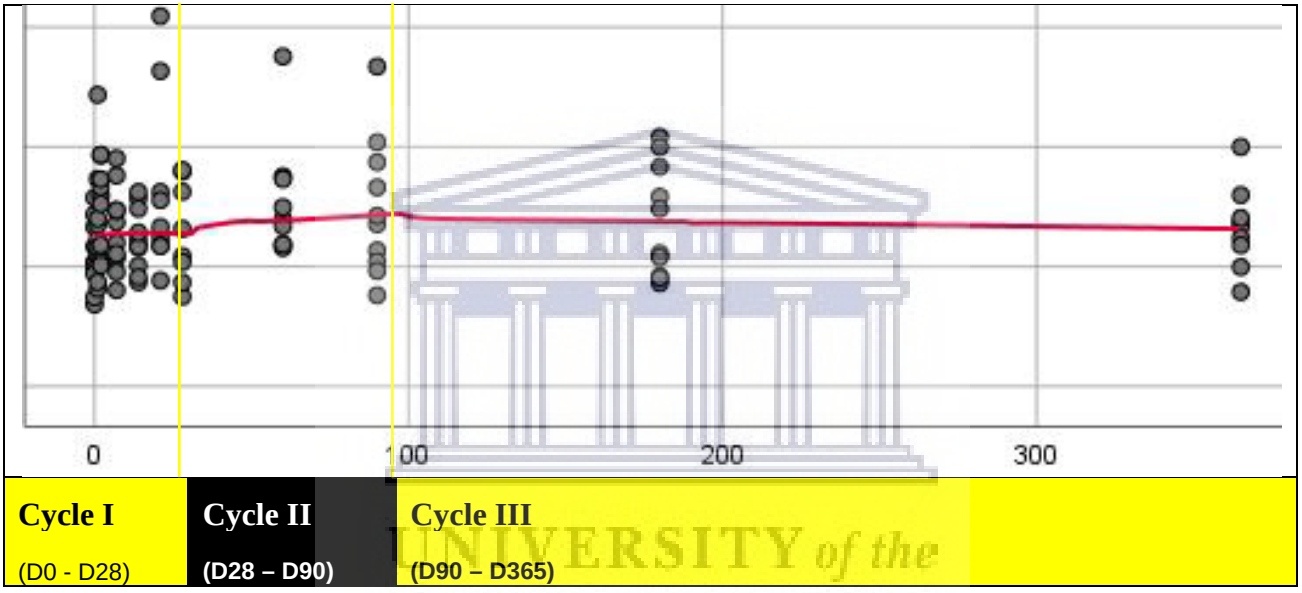


Figure (5.5): Showed the fluctuation in Ra changes over the period of time in acidic media.

- ***Cycle I:***

The initial outcome of this research showed an increase on day 1 (21.2%) and day 2 (25.1%) followed by reduction in Ra on day 7 by (8.8%). Then the cycle of Ra was repeated again to show an increase in the mean Ra percentage on day 14 (0.1%) and day 21 (75.5%) respectively, followed by a reduction on day 28 by (3.9%). The results of the present study are similar to the results of Yip *et al.* (2004) that showed an increase in the surface roughness of the Vitremer when immersed in artificial saliva for a period of six weeks. In particular, their results showed that the mean surface roughness was

increased from 0.14 µm, at the beginning of the experiment, to 0.33 µm after six weeks (Yip *et al.,* 2004). However, one of the main differences between the present study and Yip *et al*. (2004) study is that a specific intervention was done to the Vitremer specimens. The authors treated the surface of the Vitremer with 1.23% of the acidulated phosphate fluoride gel (Yip *et al.,* 2004). The fluoride could affect the surface roughness because it competes with the carboxylic anion as mentioned earlier, thereby acting as a confounding factor in the end result of the surface roughness of the material. However, this variable needs more investigation in future because we did not measure it in the present study. Furthermore, the mechanism of release of fluoride differs from other ions.

Furthermore, it is important to mention that the finding of the present study is consistent with the finding of Beresescu *et al.* (2015) who measured the surface roughness of Vitremer after a month of immersion in artificial saliva. However, the baseline Ra values were not stated by the author and thus cannot be compared to the findings of the present study. Furthermore, Beresescu *et al.* (2015) covered the specimens with the finishing gloss and this was not the same methodology as conducted in the present study. Furthermore, they measured the arithmetic mean by taking the mean from 10 different parallel lines which is slightly different to the current methodology. In addition, they did not justify why the surface roughness values had reduced in the second and fourth week after their increase in the first week. Furthermore, they did not justify the behavior of each material separately in their discussion and did not provide a specific reason for that behavior. Likewise, the outcome of this study is consistent with a study by Honório *et al*. (2008) that aimed to compare the wear of Vitremer after immersion in acid and saliva for one month in bovine specimens. The results showed that specimens that were immersed in acid had a significantly higher wear (0.5 µm ± 0.05) in relation to their respective control in saliva media (0.4 µm ± 0.07). However, justification of this finding by Honório *et al*. (2008) was the ability of the acid to dissolve the matrix is inconsistent with justification of this study. This could be related most probably to the short duration of their study. In the Honório *et al.* (2008) study, the calibration was conducted with the use of a reference specimen and covered with nail varnish. Hence, this method could be slightly inaccurate. The method of polishing of the baseline

reference specimen will not provide a 100% smooth surface and hence could have confounded their results.

The finding of the present study is inconsistent with Paula *et al.* (2014) who measured the Ra of Vitremer over a period of a month. Paula *et al.* (2014) did not find any significant change from the baseline values. There was actually a reduction in the mean percentage of Ra by (14.9%).

- ***Cycle II and Cycle III:***

The current findings showed an increase in the mean percentage on day 60 (21.4%) followed by a reduction on day 90 by (12.1%). Thereafter, the percentage of the mean Ra showed an increase on day 180 (4.1%) and day 365 (30.1%). No long term study was found in the literature with which to compare the findings of the present study. Therefore, evidence is lacking and high quality research is needed.

In conclusion, there is a wide variation in the literature on the methods of conducting the surface roughness and wear of Vitremer. Differences in the type, concentration, pH of the solution, formulations of artificial saliva and the follow up period of the samples, were noticed as well. As shown in **Table (5.4)** below this makes the standardization difficult. However, as Prakki *et al.* (2005) concluded, in order to properly detect the mechanical properties of any polymer based restorative materials, it is better to use a weak acid for a longer duration of time. Prakki *et al.* (2005) considered this as the best method to resemble the *in vivo* condition. Hence, more clinical studies are needed to generalize this fact to the clinical practice.

Evidence regarding the immersion of Vitremer in saliva media is lacking and conflicting. Furthermore, there is wide variation in the literature on the duration of the study periods, formulations of artificial saliva used and its pH. The closest formula to the present study is that of Paula *et al.* (2014).

Table (5.4): Shows the reported studies with different formulations of artificial saliva solutions that were used to measure Ra of Vitremer restorative dental material.

Author	Study title	Artificial saliva formulations	Result of change in Ra
The present study	Comparative *in vitro* study of selective physical properties of Activa, Cention N and Vitremer	Calcium 1.5 g, phosphorus 0.8833 g, potassium chloride 111,825 g, 1 litre of water Full strength HCL was used to adjust the pH to be 7.	There was a total increase in the overall mean percentage of Ra of Vitremer over the period of one year (15.4%). The pattern change in Ra showed fluctuation in mean percentages of surface roughness between increase and reduction through the study time periods. In particular, there was an initial increase on day 1 (21.2%) and day 2 (25.1%) followed by reduction in Ra on day 7 by (8.8%). Then the cycle of Ra was repeated again to show increase in mean Ra percentage on day 14 (0.1%) and day 21 (75.5%) respectively, followed by reduction on day 28 by (3.9%). Likewise, an increase in the mean percentage on day 60 (21.4%) followed by reduction on day 90 by (12.1%). Then after that, the percentage of mean Ra showed increase in day 180 (4.1%) and day 365 (30.1%).

(Beresescu *et al.,* 2015)	*In-vitro* study regarding the wearing of glass ionomer cements	0.4 g of NaCl, 0.4 g KCl,0.795 g of $CaCl_2H_20$, 0.69 g of NaH_2PO_4 , 0,005 g of Na_2Sx9H_20 , 1 g of urea and 1000 ml of distilled water NaOH and HCL were used for pH adjustment to 3, 7 and 9 in a volume of 1L.	There was an increase in Ra in both neutral and acidic artificial saliva between day 1 and day 7 followed by reduction in Ra on day 14 and day 28. The baseline measurement was not mentioned in the article • In pH = 3, Ra on day 1 = 0.63 µm, day 2 = 0.69 µm, day 14 = 0.61 µm, day 28 = 0.55 µm • In pH = 7, Ra on day 1 = 0.48 µm, day 2 = 0.76 µm, day 14 = 0.58 µm, day 28 = 0.54 µm
(Paula *et al*., 2014)	Influence of chemical degradation on the surface properties of Nano-restorative materials	- Calcium (0.1169 g of calcium hydroxide/L of de-ionized water). - 0.9 mM of phosphorus and potassium (0.1225 g potassium phosphate monobasic/L of de-ionized water. - 20 mM TRIS buffer (2.4280 g TRIS buffer/L de-ionized water).	No significant difference was noticed in Ra of Vitremer (reduction by 14.9%) for the period of one month.

(Beresescu *et al.,* 2011)	Effect of artificial saliva on the surface roughness of glass ionomer cements	The same formulation as the above study (Beresescu *et al.,* 2011) and the pH was adjusted to three different pH through the same mechanism	The results of Tukey test showed that Ra of Vitremer in distilled water = 0.079 µm. In basic artificial saliva (pH = 9) =0.0712 µm, while in acidic media (pH = 7) = 0.0714 µm or in (pH = 3) = 0.0889 µm after immersion for a month The baseline measurement was not mentioned in the article
(Honorio *et al*., 2008)	Effect of prolonged erosive pH cycling on different restorative materials	Formulations of artificial saliva were not mentioned. The pH of artificial saliva was not mentioned as well.	Ra was significantly increased to the mean percentage of (0.4% ± 0.07 SD).
(Yip *et al.,* 2004)	Effect of artificial saliva and APF gel on the surface roughness of newer glass ionomer cements	0.05 M acetate buffer with 2.2 Mm $CaHPO_4$. The solution was adjusted through the use of acetic acid to pH of 5.	Ra was increased by 60% from the baseline after 3 weeks. This percentage of increase was reduced to 42% from the baseline after 6 weeks.

5.2.2. Association of ACTIVA bio-ACTIVE-RESTORATIVE surface roughness changes

The findings of the present study showed that when *Activa bioactive restorative had been immersed in acidic media* there was a non-significant positive association in the surface roughness after one year of immersion ($p = 0.633$). The percentage of increase in acidic media was found to be (6.99%) from the baseline. In particular, there was a fluctuation that showed cycles of increase and reduction in Ra. Increase in Ra values was noticed on day 1 (9.5%), day 2 (2.9%), day 7 (9.1%) and day 14 (2.6%). Then reduction was noticed on day 21 by (0.4%). And increase in Ra was noticed again on day 28 (5.9%). Then, reduction in Ra again on day 60 (4%), and day 90 (1.6%) was followed. Then increase again on day 180 (24%) and day 365 (21.1%). Likewise, *for artificial saliva,* the positive association was found to be insignificant as well ($p = 0.201$). The increase in mean Ra percentages was found to be (5.03%). Except for day 7 where there was reduction in Ra by (8.5%), there was an increase in mean Ra percentages for all measured periods of time as follows : day 1 (1.3%), day 2 (4.2%) ,day 14 (2.2%) , day 21 (0.54%), day 28 (4.1%), day 60 (0.04%), day 90 (3.5%), day 180 (14.1%), day 365 (28.7%).

This could be interpreted as follows: immersion of Activa material; whether in acidic or saliva media, showed no significant change in the surface as shown in **Figure (4.15)**. In the early days of immersion, it is important to mention that although the Ra was increased in both media, Activa gained weight in acidic media while it lost weight in saliva media. Although there is a period of water sorption in both acid and saliva media at the beginning of the experiment, however, in acid media there is an increase in weight accompanied by an increase in Ra due to an imbalance in the osmotic pressure. Consequently, this would lead to an influx of water through the particles which could become more porous as depicted on the SEM for the post-experimental image in acid media in **Figure (4.26)**. Furthermore, increase in Ra in the early days could be linked to dissolution of silica from the periphery of glass particles by the acid solution. This assembly will lead to the bond breakage of the silica backbone which could result in local release of Si-(OH) and hence, formation of the silica gel that could lead to final changes in the surface topography (Maeyer *et al*., 1999). The bond is more vulnerable

to breakage in acidic media than in saliva media due to the direct action of the lactic acid (Vogler, 1998). Therefore, partial dissolution of the material will take place. Roulet *et al.* (2020) mentioned that the increase in Ra could be due to leaching of ions from glass, such as calcium. It is important to mention that the primary effect of fillers in acidic media is related to the release of network dweller ions facilitated by the presence of the liquid i.e. introduction of the surface reaction of the bioactive material in the presence of the absorbed water in the polymer network (Maeyer *et al*., 1999).

On the other hand, immersion of Activa in saliva media led to loss of weight after the period of water sorption. This weight loss was associated with an increase in Ra and could be justified by slight degradation of the rubberized ionic resin matrix which could be responsible for the increase in weight and the Ra in saliva media. Furthermore, the concentration gradient of ions was usually higher in this bioactive material when compared to ions in artificial saliva. In the long term, there are two main factors that could explain the mild changes in the long term;

- ***Effect of the structure as seen under SEM***

Although the structure of these fillers was not stated by the manufacturer, some information was provided by the material safety data sheet and the FDA report (2012) as seen earlier in **Table (3.1)**. Hence, there is a lack of information on whether the structure of methacrylate is the HEMA component of Vitremer or if the di-urethane group affects its property to resemble Cention N. Hence, further research is needed. However, recently, only one elemental analysis was published about the elements of Activa (Ruengrungsom *et al*., 2020). Hence, it cannot be concluded that each type of filler could originate from one paste system. Three types of fillers were depicted in the SEM in **Figure (4.26)** of the present study through differences in the backscattering property. The images of the present study are in accordance with Tiskaya *et al.* (2019) SEM findings. However, Tiskaya *et al.* (2019) explained that there were only two types of filler particles. However, Ruengrungsom *et al.* (2020) recently contradicted this finding by mentioning that Activa has five types of fillers, three of them are irregular and the other two are oval and spherical respectively. However, the SEM image was missing from the Ruengrungsom *et al*. (2020) study for correlation of the EDS data

analysis with the image of the SEM. Yet, it is possible to compile the five types into three types only. The three types that could be extracted from the Ruengrungsom *et al.* (2020) table are: 1) bioactive glass (calcium fluoroaluminosilicate glass that contains phosphate, 2) calcium-barium-aluminum-phosphate particles, 3) calcium-barium-aluminum particles; the author reported that this type does not contain phosphate. Furthermore, Ruengrungsom *et al*. (2020) believed that Activa does not contain Ytterbium. However, further research is still needed due to the fact the evidence is lacking and inconclusive. In addition, no information was found about the presence of any coupling agent or initiators in the Activa structure in the literature. The evidence is lacking about Activa's degree of conversion as well.

- ***Effect of the size of the particles***

The pre-experimental SEM images of the present study **Figure (4.26)**, showed variation in the size of the particles. This is consistent with the SEM images of Roulet *et al*. (2020) who mentioned that Activa had an irregular filler shape when mechanical load wear was applied to investigate the surface. However, his investigation on wear was only done for a short period. Furthermore, for the specimen of Activa that received the dual curing technique, the light was applied for only 20 seconds, which contradicts the time of curing of the present study. The authors also did not mention why they placed the materials in water for three weeks before taking the impression of the surface. Contrary to the image of the acidic media, the post-experimental image of the sample that was immersed in artificial saliva media for a one year period was similar to the pre-experimental image (before immersion).

While the SEM of Activa showed the presence of nano-size particles, these small particles were distributed in very high percentages as depicted in the SEM images in **Figure (4.26).** Khan *et al*. (2019) mentioned that nano-particles could provide good mechanical interlocking with the polymer matrix. Furthermore, nano-particles have a significantly larger surface area that transfers the load from the polymer matrix to the nano-particles, therefore reducing the chances of wear (Zhao & Xie, 2009). This could give an explanation for the good integration between the matrix and fillers in the pre-experimental image, as well as the post-experimental one, especially the saliva image.

Nano-fillers have the ability to maintain the polished surface for a long time (Khan *et al.,* 2019). Therefore, those fillers were also shown to hinder the disintegration and dissolution of the outermost layer of the material (Khan *et al.,* 2019). Consequently, the resultant surfaces become densely packed. The packing of the fillers is actually not influenced only by filler size but also filler shape, arrangement and distribution (George, 2011).

It was also noticed that Activa did not show any cracks on the surface post-experimentally, whether in acid or saliva media. The rationale could be related to the fact that the presence of nano-fillers led to reduction of the inter particle distance; hence led to reduction on the load bearing stress. Therefore, the probability of crack formation is reduced (George, 2011; Khan *et al.,* 2019). Therefore, all these factors provide better resistance and high optical properties as well. Release of nano-size filler particles should also be considered due to the fact they could easily elute more than the larger particles. Hence, this increase in Ra is not significant and changed slightly from the baseline.

The finding of the present study is consistent with Latta *et al*. (2020) who measured the localized and generalized wear of Activa. Latta *et al.* (2020) found generalized and localized wear of Activa; generalized wear loss equal to (0.268 ± 0.059 mm^3) as well as localized wear loss (0.338 ± 0.56 mm^3). It is important to mention that this author did not report baseline values in order to measure the percentage. Hence, Latta *et al*. (2020) concluded that wear values of Activa are comparable to Fuji Equia Forte and the newly developed resin composite ASAR-MP4. In addition, Latta *et al.* (2020) categorized Activa as a ‘’bioactive resin-modified glass ionomer cement” and proved it had better resistance to wear than the traditional RMGIC (Fuji II LC). The major difference between the Latta *et al.* (2020) study and the present study is the measuring of the mechanical wear instead of the chemical wear.

5.2.3. Association of Cention N surface roughness changes

The findings of the present study showed that *the association of the Ra of Cention N in acidic media* was found to be positive (p = 0.000). This increase was significant over a period of one year. There was a total increase in Ra by (15.2%) from the baseline. In

particular, throughout the days, changes occurred in cycles; there was an initial increase in mean percentages of Ra in day 1 (34.5%), 2 (12.3%) and 7 (15.9%) followed by a reduction in day 14 by (1.2%). The cycle repeated again with an increase in day 21 (42.8%), day 28 (18.2%), day 60 (9.7%), day 90 (20.9%) followed by reduction in day 180 by (12.8%). Then, a final increase on day 365 was found to be (15.2%). These cycles explain wearing of the thickness of the surface layers. However, this positive association was not significant when Cention N was immersed in artificial saliva media (p = 0.154). Increase in the surface roughness in acidic media could be justified by the ability of the acid to erode the surface, causing significant change from the baseline. Therefore, the rate of degradation of particles is higher in acidic than in saliva media. Yao *et al.* (2020) mentioned that this could be linked to release of some ions, particularly calcium. Furthermore, Tiskaya *et al*. (2019) explained this fact by the ability of the acid to hydrolyze the Al-O-Si bonds more in comparison to the situation under a neutral condition. This is due to the fact that these bonds stay intact under the neutral media such as artificial saliva when the pH was equal to seven (Tiskaya *et al.,* 2019). Furthermore, in the acidic media the concentration of the hydrogen proton was increased when compared to neutral artificial saliva media (Tiskaya *et al.,* 2019). Consequently, the release of calcium ions that would replace the hydronium ions increases as well. This is due to the fact that lactic acid is a weak, uncharged acid and both the reactants and products in the following equation will be in equilibrium. However, although Maeyer *et al*. (1999) mentioned that calcium is a strong cationic ion and one of the network dweller ions that could render the media basic, Tiskaya *et al.* (2019) stated that calcium is released in large amounts especially in the early days of Activa immersion.

Another reason that could justify the ability of Cention N to neutralize the media is the release of the alkaline fillers. It seems that the alkaline fillers could adjust the pH of the solution but not for a very long time. This could clearly explain why the association became significant in the acid but not in the saliva.

On the other hand, the positive *association of Ra in saliva media* was found to be insignificant (p = 0.154). The mean total increase in Ra was found to (23%) from the

baseline. A fluctuation was noticed in mean Ra percentages. In particular, the percentage in each period of time was found to be as follows: there was an initial increase in mean percentages of Ra in day 1 (117.3%), followed by reduction in day 2 (6.8%). Then, an increase was noticed in day 7 (93.7%) and day 14 (10.8%) with a reduction in day 21 by (14.4%). The cycle repeated again with an increase in day 28 (16.5%), day 60 (9.1%) followed by a reduction in day 90 by (13.9%). Lastly, an increase in day 180 (23.8%) followed by a reduction in day 365 by (5.7%).

This total increase, although is not significant, could relate to the hydrophobic effect of the UDMA. UDMA was reported to be the main component of the matrix (Todd, 2016). This monomer is hydrophobic in nature and therefore resistant to the softening effect. Hence, there is a marked reduction in the release of fillers to the solution due to the fact that the matrix could stay rigid and hard. Another factor that could be taken into consideration is the variation in the size of the particles as claimed by the manufacturer (0.1 µm - 35 µm) and clearly seen under the SEM in **Figure (4.27)**. Placement of the finer particles between the larger ones could lead to reduction in the inter-particle spacing which makes the material less susceptible to wear. These fillers, when mixed together, would provide more matrix-filler interaction and hence could explain why Cention N had lower Ra Values in saliva media when compared to Vitremer that had larger particles (around 0.3.µm) as seen in the SEM, **Figure (4.25)**. Furthermore, Osorio *et al.* (2016) reported that the percentage of fillers by volume in Cention N is higher than in Vitremer. Furthermore, the SEM images of the present study are consistent with the findings of Tiskaya *et al*. (2019) and Yao *et al.* (2020) who stated that the nano-fillers in Cention N could be mainly yttrium fluoride (Tiskaya *et al*., 2019; Yao *et al.*, 2020). Tiskaya *et al.* (2019) mentioned that the dominant particles released during the first six weeks of immersion were calcium fluorosilicate particles. This could be consistent and clearly seen under the SEM of the present study as large size fillers with differences in the back scattered property **Figure (4.27).** This type of glass resembles the bioactive glass in Activa but it does not have any phosphate component (Tiskaya *et al.,* 2019).

After that, Tiskaya *et al.* (2019) mentioned that the release of ionomer glass particles and the rest of the calcium fluorosilicate glass would follow. However, until the end of

their experiment, the authors thought that barium-alumino-silicate inert glass and YbF_3 remained intact. However, this point needs further study due to the fact that the SEM is a two dimensional image and hence the actual size of the particles is not fully determined. Recently, Ruengrungsom *et al.* (2020) revealed the elements of Cention N. Ruengrungsom *et al.* (2020) found that the opaque white color represented ytterbium tri-fluoride (YbF_3) fillers (Roulet *et al.*, 2020; Ruengrungsom *et al*., 2020). Furthermore, from the images, the nano-size particle is mostly seen in (YbF_3) particles, although some particles of this type had been shown in micro size level as in a post-experimental acidic sample. The same author had mentioned that the dark grey showed the calcium fluorosilicate glass and the light grey showed the Ca-Ba-Al silicate glass (Ruengrungsom *et al*., 2020). The fourth one is the Ba-Al silicate glass which is the darkest filler among the whole fillers. It is shown in the SEM below with different sizes.

In the present study, as the specimens of Cention N aged under the constant effect of the solutions, such as in day 365, there was an increase in Ra by (5.7%) from the baseline. This could mainly be related to the degradation of the matrix. Furthermore, it could be related to the fact that there was a rapid release of free radicals as it reacts with oxygen in water (Toledano *et al.*, 2003). In addition, Cention N when compared to Activa is mixed at a ratio of 4.6:1. A higher mixing ratio could limit the mobility of the free radicals and consequently will reduce the rate of polymerization (Panpisut & Toneluck, 2020). That is why the surface roughness was higher, especially in the first days, for both acid and saliva specimens. It is important to mention that no cracks were found in the post-experimental image depicted in the SEM in **Figure (4.27)**. The absence of cracks in Cention N could be explained by the variations in the size of the particles. Hence, the smaller particles usually occupy the spaces between the larger particles. Consequently, this will lead to a reduction of the stress concentration and extend the surface fatigue limit of the cement (Zhao & Xie, 2009).

No single study was found in the literature about the Ra of Cention N and immersion in any liquid solution: whether acid or saliva. However, Mazumdar & Chowdhury (2018) measured the Ra of Cention N after applying mechanical intervention (brushing) for sixty minutes using the same sample size as the present study (n = 10). Although

Mazumdar & Chowdhury (2018) mentioned that there was a significant change in Ra values of Cention N and found it comparable to Ra values of nano-composite; no values were mentioned in the article. In particular, the mean baseline surface roughness value, values at the end of the experiment and percentage of change in Ra of Cention N samples were not mentioned. Hence, the consistency of the Mazumdar & Chowdhury (2018) study with the present study cannot be determined due to the poor quality of the study.

5.2.4. Comparison of the surface roughness between the three restorative materials

The findings of the present study showed that when the Kruskal-Wallis test was used for *comparison of Ra in acidic media between the three materials*, the results showed a significant difference between the materials in the early days of immersion; day 1 (p = 0.037), day 7 (p = 0.044) and day 14 (p = 0.022) in relation to the baseline (day 0). Actually, Vitremer was found to be the highest in surface roughness followed by Activa while Cention N was found to be the least at these three periods of time. However, Vitremer was found to be significantly higher than Cention N in these three periods of time. This could be explained by the large size of the Vitremer particles as well as the difference in the compositions. Moreover, there is an absence of a phenol ring in this main component, or UDMA could enhance the toughness and flexibility when compared to HEMA or Bis-GMA of Vitremer. This would make the UDMA monomer more reactive with a higher degree of conversion. Furthermore, partially aromatic di-methacrylate (TMX-UDMA) in Cention N also had a higher degree of double bond conversion than the Bis-GMA of Vitremer. Furthermore, the TMX-UDMA monomer has an aromatic group which gives the structure of Cention N additional stiffness (Moszner *et al.*, 2008). Consequently, the matrix becomes more resistant to wear and this would lead to less release of the monomer as well.

After that, as the three materials aged in acidic media, there was a change in the ranking of the three materials; Vitremer still the highest, followed by Cention N followed by Activa. Actually, Activa was reported to have the least Ra among the three materials at the end of the study. The Kruskal-Wallis test showed a difference between the three materials at day 180 (p = 0.01). This means in the long term, Cention N was susceptible

to wear by acid more than Activa. However, the difference between them was not significant. On the other hand, Vitremer was found to be significantly higher in terms of surface roughness when compared to both Cention N (p = 0.000) and Activa (p = 0.005). Vitremer has significantly higher Ra than Activa due to the release of a higher particle size in comparison to Activa reported under the SEM. Furthermore, there is marked disintegration between the matrix and fillers in the post-experimental image under the SEM in **Figure (4.25)**. However, a comparison between the composition of Vitremer and Activa was not made due to the fact that the composition of Activa is not well stated by the manufacturer. On the other hand, Cention N was found to be significantly higher which might be due to larger variations in the size and shape of the particles in comparison to Activa. Cention N has very irregular shaped particles. As stated by Khan *et al.* (2019) irregular shaped particles usually possess lesser packing ability and hence lesser retention when compared to the homogenous and spherical particles of Activa. This is clearly seen under the SEM for Cention N and Activa in **Figures (4.26) and (4.27)**. This is consistent with Tiskaya *et al*. (2019) who found that the average particle size of Activa is less than 10 µm under the SEM. Another factor which could be related to the rate of release of ions was mentioned by Tiskaya *et al.* (2019); the rate of release of Calcium and Aluminum in Activa was found to be slower than the rate of calcium of Cention N.

On the other hand, comparison of *the surface roughness of the three materials when immersed in artificial saliva media* showed insignificant differences in terms of Ra between the three materials. This finding of the present study is inconsistent with Roulet *et al.* (2019) that compared the wear of Cention N to Activa when both of them were stored in water for a short period of time (three weeks). The authors found that Cention N had a higher amount of wear when compared to Activa. In particular, the wear of Cention N was equal to 2.455 ± 0.242 mm^3 while Activa was around 1.571 ± 0.228 mm^3. The difference was found to be significant after the 400,000 load cycle. Furthermore, Roulet *et al*. (2019) found that the wear behavior of Cention N and Activa resembled the wear of flowable composite. However, Roulet *et al.* (2019) did not apply any light-cure to the specimens. Furthermore, the author assumed that Cention N is a

composite resin and at the same time they did not apply the light-cure because they did not want to confound the results, which was a bit misleading.

5.3. Limitations of the study

A high quality randomized control trial is required to support the findings of this *in vitro* study due to the difficulty in simulating all the oral conditions in a single laboratory study. In addition, there is a need for more *in vitro* studies to integrate the influence of other parameters such as; drawing a comparison between the ions that are released from each material, the type and the percentage of release of the monomers from each material in both media. Furthermore, based on the results of the present study, other limitations are listed below;

- The release of the un-reacted monomer has a direct relation with the degree of conversion. Hence, the degree of conversion affects the mechanical properties tested. However, one of the limitations of this study was that the degree of conversion was not determined.
- It has been mentioned in the literature that use of constant shaking will provide more reliable results and distribute the effect of the acid and saliva on both sides of the specimens. The specimens in the present study were immersed into the solutions and remained dormant during each period of the study.
- During the establishment of the polishing of the present experiment, the baseline Ra values for all three materials were high. This could be related to the use of 800 grit paper which could provide a higher degree of surface irregularity at the onset, although polishing was performed by a single investigator. Hence, it is recommended that the specimens should be polished with finer grit papers only: 1000, 1200. However, the latter method is time consuming.
- Although liquids were changed during each period of time and no cross contamination occurred between the specimens, the presence of environmental fungus after completion of the third month indicates that conducting this *in vitro* experiment in aseptic conditions should be a priority. This is highly recommended in order to rule out the confounding effect of the toxic products secreted by the microorganisms that could be present in the working field as well as in the

specimen jars for the extended period of the study. The organisms and their products could affect the pH of the media.

- The authors used litmus paper to determine the level of the pH for the acidic and saliva solution that *w*as mixed in the lab. Although the use of litmus paper with the indicator colours was sufficient in this study, recent literature recommends the use of a pH meter in future *in vitro* studies, as it gives a more accurate reading.
- For the SEM images, a new sample from each material was prepared for the pre-experimental SEM images. The new samples were prepared from the same batch and under the same experimental conditions regarding the temperature and relative humidity. Furthermore, the powder and liquid were weighed before mixing. However, the major aim for conducting the qualitative analysis in the current research was to provide more investigation concerning the surface of the studied materials.
- One of the specific objectives of the present study was to measure fluoride release of the three studied materials and to draw a comparison between them in terms of this objective as well as to link it to other studied physical properties. However, fluoride was not measured due to technical challenges, in particular, the inability to control the pH of the collected solutions. Therefore, the experiment could not be completed.

CHAPTER VI: CONCLUSION AND RECOMMENDATIONS

Within the limitation of the study it can be concluded that:

1. The acid solution that was prepared *in vitro* was able to cause changes in the weight and the surface roughness of the restorative materials over the study period.

2. Vitremer was found to be the highest material that loses weight, and height especially when immersed in acidic media. However, dimensional changes in other materials (Cention N and Activa) were insignificant when compared to the baseline.

2. Vitremer showed the most significant surface roughness changes after the immersion in the acidic solutions. Although all materials under study showed changes, these alterations occur over a long period of time (one year) which suggests all the materials are suitable for clinical practice.

3. Activa showed the lowest roughness values, no significant changes in the weight and height even when subjected to the acidic attack for a year.

4. Although the process of weight, height and change in surface roughness could be more complex in the clinical setting, due to the effect of multiple additional variables, *in vitro* models provide the fundamental mechanism of biodegradation of the selected materials.

The clinical significance of findings of the present study:

All the materials studied were subjected to dimensional and Ra changes due to long-term exposure to acidic substances, but the newer materials (Activa and Cention N) seemed to be less affected than the older, well-known material (Vitremer) which may influence the clinician's choice of restorative material for use in pediatric dentistry.

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APPENDICES

Appendix A: Ethical approval

1.1. Dr RM Jafar (Dentistry)

Study project: Comparative *in vitro* study of selected physical properties for Activa, Cention N and Vitremer.

Registration number: BM18/9/6

Ethics: *Approved*

Appendix B: Data collection sheet

The page is inserted in the following page and was copied 10 times in order to fill the data in each period of time.

	Materials																																																									
	Vitremer																				Activa																			Cention N																			
	Artificial saliva										Acidic solution										Artificial saliva										Acidic solutions									Artificial saliva										Acidic solutions									
Sample code	C1A	C2A	C3A	C4A	C5A	C6A	C7A	C8A	C9A	C10A	C1b	C2b	C3b	C4b	C5b	C6b	C7b	C8b	C9b	C10b	V1A	V2A	V3A	V4A	V5A	V6A	V7A	V8A	V9A	V10A	V2B	V3B	V4B	V5B	V6B	V7B	V8B	V9B	V10B	A1A	A2A	A3A	A4A	A5A	A6A	A7A	A8A	A9A	A10A	A1A	A2A	A3A	A4A	A5A	A6A	A7A	A8A	A9A	A10A
Ra (day 0)																																																											
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Appendix C: The SEM images at different magnification levels

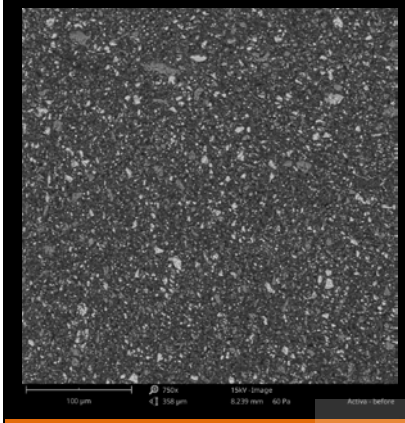
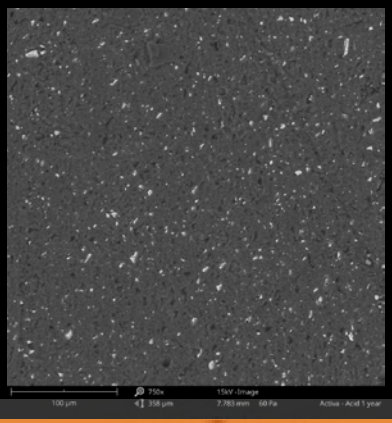
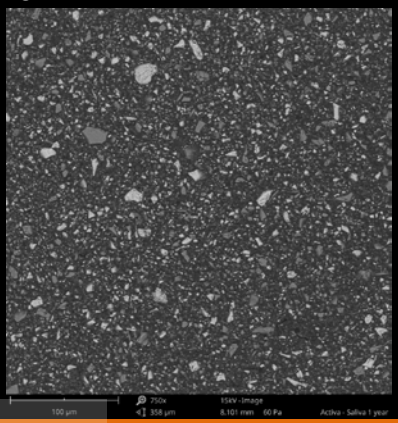
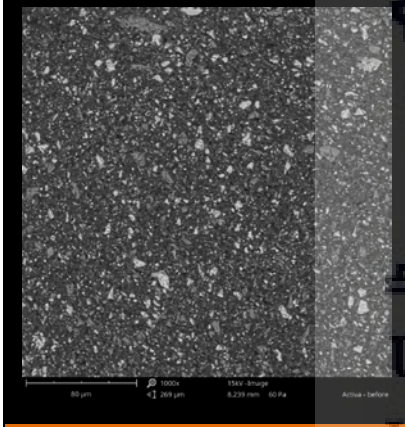
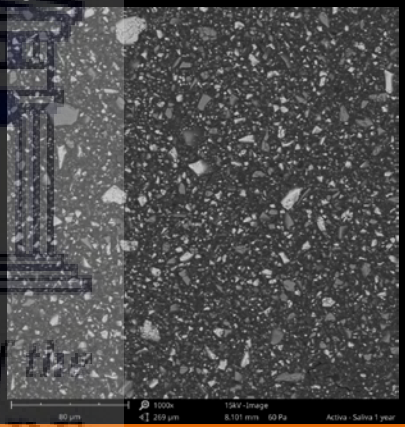
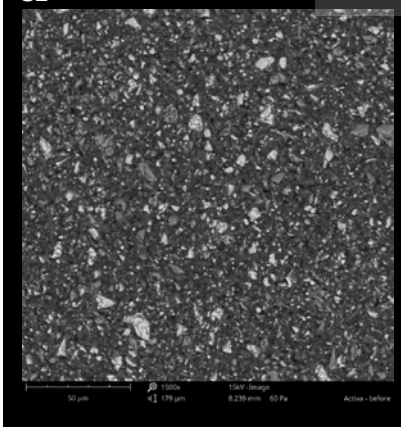
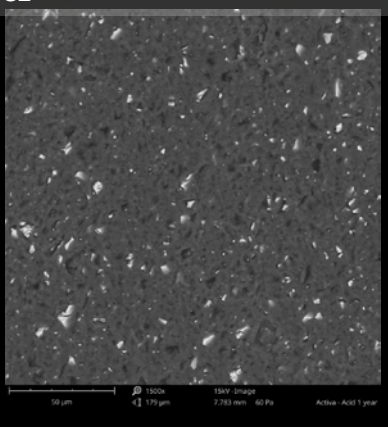
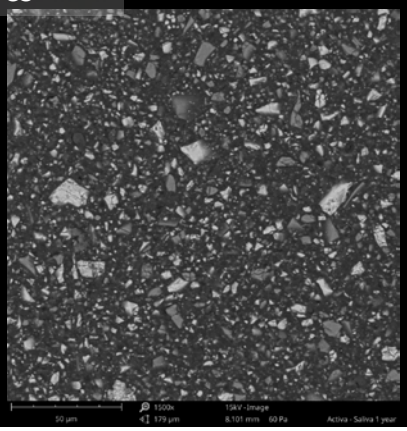
The images were presented in this appendix in the following order:

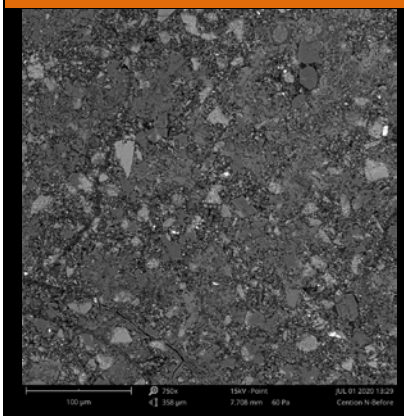
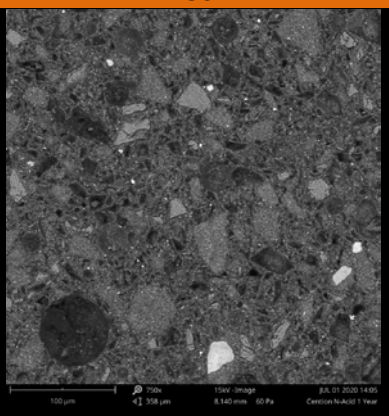
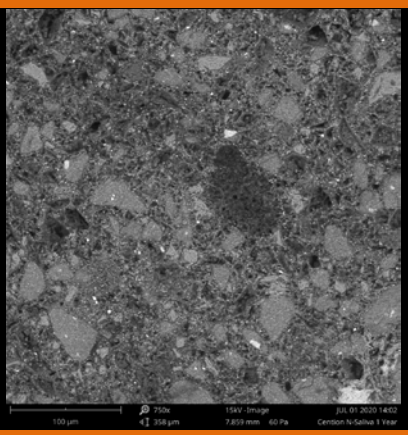
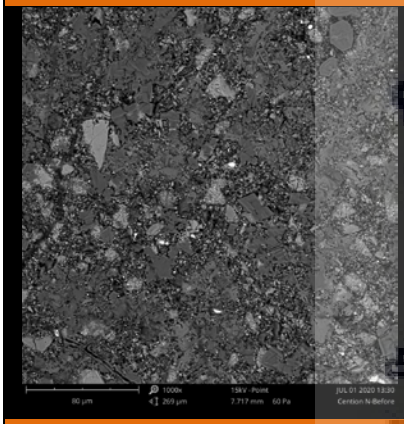
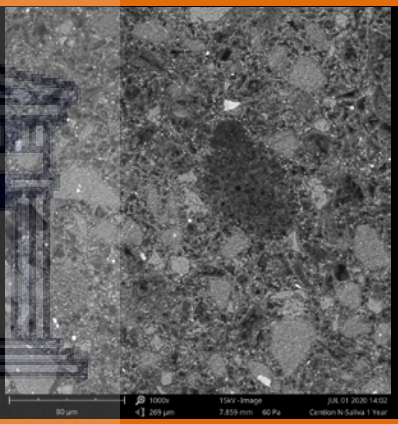
1. Vitremer

2. Activa

3. Cention N

Vitremer Before immersion	Vitremer in acid after a year	Vitremer in Saliva after a year
750 X		
A1	A2	A3
1000 X		
B1	B2	B3
1500 X		
C1	C2	C3

Activa Before immersion	Activa in acid after one year	Activa in Saliva after one year
750 X		
A1 	A2 	A3 
1000 X		
B1 	B2 	B3 
1500 X		
C1 	C2 	C3 

Cention N Before immersion	Cention N in acid after one year	Cention N in Saliva after one year
750 X		
		
1000 X		
		
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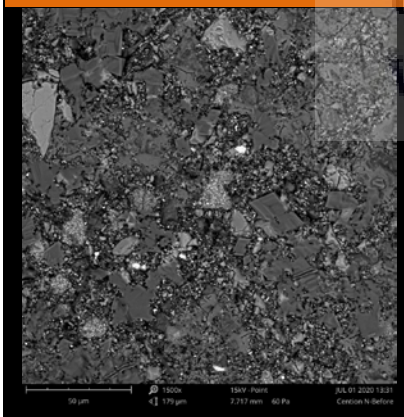		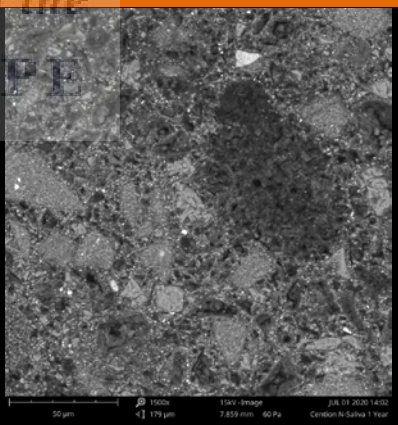

Appendix D: Turntin Report