Mechanical Properties of Glass-Ionomer Cement Composited by ZrO_2 and $CaMgSi_2O_6$

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Abstract

Glass ionomer cements (GICs) are widely utilized in clinical restorative dental applications, which suffer from poor mechanical strength. Recent research shows that GIC achieves optimal performance when modified with lower percentage of filler materials, particularly when using nanoparticles, due to the resultant increase in surface area and packing density of the cement. Notably, while some fillers enhance the mechanical properties of the cement, others fail to provide improvements. This study addressed a gap in the literature by investigating the impact of acidic/basic additives, such as diopside ($CaMgSi_2O_6$) and zirconia (ZrO_2), on the properties of the cement. The reactivity of zirconia and diopside differ distinctly from traditional calcium-aluminosilicate glass when exposed to acidic conditions in GICs. Also, to clarify the impact of filler's acidity/basicity on filler reactivity during cement setting, the potential for mechanical enhancement by using nano-sized particles is generally limited to the submicron scale. This research incorporated diopside at concentrations of 2, 4, and 6 wt.%, and zirconia at concentration of 8, 10, and 12 wt.% into a glass powder component. Results demonstrated that adding 8 wt.% zirconia led to a 49% enhancement in compressive strength, also improve microhardness by 16 %, attributed to its non-reactive nature, minimal dissolution, and high inherent strength of ZrO_2. In contrast, diopside had a detrimental effect due to its basic nature compared to that of glass powder. The base cement exhibited a setting time of 6.5 min, which slightly increased to 7.4, 7.6, and 7.9 min with the addition of 8, 10, and 12 wt.% zirconia, respectively, while diopside additions at 2, 4, and 6 wt.% resulted in more pronounced increases to 8.3, 8.7, and 9.1 min. Zirconia showed better potential as a reinforcing filler, while diopside, due its basicity, was less effective in enhancing mechanical performance.

Keywords: ZrO_2, Diopside, Glass Ionomer Cements, Mechanical Properties, Dental Materials.

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1- Introduction

Nowadays, there are different solutions for the treatment and repair of teeth. In the 1900s, Amalgam was the first and strongest dental cavity-filling material, which was composed of Hg, Sn, Ag, and Cu [1-3]. However, two major drawbacks of using amalgam in dental restoration are its improper appearance, weakness in adherence to teeth tissue, corrosion, and it rarely causes mercury toxicity [2, 4]. Recently, due to the emphasis on the beauty of teeth, patients prefer to use materials that are compatible with real tooth anatomists [5, 6]. Therefore, due to the demand from patients, scientists consider glass ionomer cement (GIC) and dental composites as the more suitable options for functionality and appearance. Dental cement, after amalgam and composites [7], is the third important category of dental repairing materials [8]. The cements are combinations of powder and liquid that convert to a pasty substance and is used as filler for cavity and caries repair. The most important dental repairing cements are GICs [9]. The competitive advantages of contemporary GICs compared to other materials include sustained release of fluoride ions [10], similarity of the thermal expansion coefficient with enamel and natural dentin, good chemical and physical adherence, and biocompatibility [11, 12]. In any case, the main defect of this restorative dental material is low mechanical strength compared to vital standards of dental materials applications [11].

Traditional GICs are formed through an acid-base reaction between aluminum silicate alkaline earth bearing glass powder and an aqueous solution of polyacrylic acid (PAA) [13]. The formation of a strong three-dimensional (3D) network within the GIC matrix is crucial for achieving high mechanical strength.

Some studies have investigated the effect of reinforcing fillers on GICs to improve their mechanical strength. Different strategies have been suggested, including the use of fibers [11, 14],

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nanoparticles [15, 16], and even micron-sized additives [17, 18]. Beyond the intrinsic properties of reinforcing particles, their nanoscale dimensions offer advantages such as increased surface area, improved void filling, and enhanced crack resistance [19]. However, the interaction between nanoscale particle size and material properties leads to complex behaviors and makes outcomes difficult to predict. Therefore, it is essential to evaluate the overall mechanical performance of GIC composites with micron-sized reinforcing particles. The evidence suggests that incorporating micron-sized ceramic powders can have varying effects on the compressive strength of GICs, with most studies demonstrating enhanced flexural strength [18, 20-22]. Predicting mechanical outcomes remains a significant challenge, as the mechanical outcomes largely depend on the type, size, and concentration of the filler used [11, 22]. These findings emphasize the importance of investigating the intrinsic properties of fillers—particularly their reactivity during the cement setting process. The setting reaction in GICs is governed by an acid–base interaction, in which different materials exhibit varying reactivity rates, affecting the kinetics and final structure of the cement matrix.

Incorporating micron-sized ceramic powders with high mechanical strength, such as yttria-stabilized zirconia (YSZ)/ZrO_2, into the glass powder of the cements and other dental materials offers a promising alternative to amalgam due to their superior strength and aesthetic properties [18, 23]. Meanwhile, some studies have shown that GICs reinforced with high hardness and strength micron-sized ceramic powders did not significantly increase mechanical strength of the GIC composites [18, 22, 24].

The strength of the resulting cement is highly dependent on the acidity/basicity or neutral of the composite materials added compared to the base glass powder. This is because the cement's structure relies on an acid-base reaction, and the nature of the added materials can significantly impact the formation and integrity of the cement network [25]. Zirconia can exhibit both acidic, basic or neutral inherent depending on the conditions and the other materials interacts with [26].

Diopside ($CaMgSi_2O_6$) is another moderately strong mineral with good hardness [27]. It is also an important bio-ceramic that contains calcium, magnesium, and silicon with a monoclinic structure [28, 29]. It has been enhanced bioactivity of the bone cement; with no sign of toxicity [29, 30]. Diopside is generally considered as a basic ceramic material because it contains calcium oxide and magnesium oxide in its structure. Due to its biocompatibility and mechanical properties, diopside is used in a wide range of clinical applications, such as bone [29] and tooth root implants [31], and drug delivery [32].

The size of the reinforcing material is very important. Agglomeration of materials at the nanoscale leads to less precise control over size distribution [33]. Therefore, the addition of zirconia and diopside powders in submicron sizes, close to the nanoscale, was proposed as an reinforing material for GICs based on their acidic/basic behaviour. Diopside exhibits a slight basic nature due to the presence of alkaline earth metal oxides, while aluminosilicate glass powder and zirconia are amphoteric, capable of reacting with both acids and bases [34-36].

This study investigated the effects of incorporating different percentages of submicron diopside and zirconia particles to GIC. The primary objective was to assess the impact of these additives on the mechanical strength of the resulting composite material. For this purpose, a glass ionomer powder based on a SiO_2-Al_2O_3-CaF_2 glass system was synthesized using the melt-quenching method. Diopside powders were synthesized via the sol-gel process. Subsequently, varying amounts of diopside (2, 4, and 6 wt.%) and zirconia (8, 10, and 12 wt.%) were incorporated into the glass powder as reinforcing materials. The mechanical properties of the prepared samples, including compressive strength and microhardness, were evaluated. Also, FTIR analysis and pH

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changes was performed on the resulting cements for better investigating and explain the role of reinforcing particles within the cement matrix after the acid-base reaction between polymer and powders. Furthermore, SEM images examine the morphological features and surface characteristics of the composite cement specimens.

2- Experimental procedure

2-1- Materials

The raw materials employed to synthesize the glass powders were high-grade SiO_2, Al_2O_3, NaF, P_2O_5, CaF_2, and TiO_2, all powders supplied by Merck Co with purities exceeding 99%. The reinforcing powders used in this research were purchased zirconia (ZrO_2, 99.6% Merck, 1314-23-4) and synthesized diopside ($CaMgSi_2O_6$). Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, 99% sigma-aldrich, 7791-18-6) and calcium nitraye tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$ 99% sigma-aldrich, 13477-34-4) was the initial materials for synthesizing diopside by the sol-gel method. Acrylic acid (AA, Merck, 79-10-7), maleic acid (MA, Merck, 110-16-7), potassium persulfate ($K_2S_2O_8$, 99% Merck, 7727-21-1) and ethyl acetate ($CH_3COOC_2H_5$, 99% Merck, 141-78-6) were utilized for synthesizing polymeric acid.

2-2- Syntesis the glass powder

The glass components were weighed meticulously, following the composition derived from the Fuji II commercial powder using XRF analysis, as outlined in Table 1. However, SrF_2 substituded with CaF_2 in the composition of glass synthesized in this study. Following this, the mixture of oxides and fluorides was heated from room temperature and gradually increased to 1500°C at a heating rate of 7°C/min. The resulted melt was soaked at this elevated temperature for 2 h to facilitate homogeneity. Finally, the molten glass was rapidly cooled in distilled water.

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Table 1. The proportions of oxidation and fluoride compounds related to glass composition.

Composition	**Al_2O_3**	**SiO_2**	**NaF**	**P_2O_5**	**TiO_2**	**SrF_2**	**CaF_2**
Fuji II-self cure	25.05	34.4	3.3	4.5	0.23	32.5	-
Glass	25.05	34.4	3.3	4.5	0.23	-	32.59

2-3- Filler materials

Zirconia and diopside powders were used as reinforcing fillers in this study. Diopside powder with submicron particle size was synthesized via the sol-gel method and further processed by planetary milling. The resulting powder exhibited high phase purity, as confirmed by XRD analysis, and displayed a particle size distribution comparable to that of the commercial ZrO_2 filler.

2-4- Co-polymer synthesis

The polymer binder was synthesized according to a procedures described in detail by Teimoory Toufal et al [37]. A polymer synthesis experiment began with preparing an initiator solution by dissolving $K_2S_2O_8$ in deionized water (DI). The reaction setup involved a three-neck reactor under inert conditions, maintained at 98°C. Solution containing acrylic acid and maleic acid with 8:1 ratio in DI along with $K_2S_2O_8$ solution were gradually added to the heated initiator solution using a dropping funnel. Following complete addition, the polymerization reaction continued for 10 h. Finally, the polymer product was purified through methanol dissolution followed by precipitation with $CH_3COOC_2H_5$ and freeze drying.

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2-5- Cement Sample Preparation of GIC composites

All GIC composites were prepared manually by mixing the synthesized glass, ZrO_2/diopside powder, and the polymer liquid with a spatula and the resulted paste set in a mold by 30 min, as described in our previous study [38]. Seven groups of composite cements, five samples for each group (a total number of 35 samples), were created and coded according to Table 2. The 0%DIO/ZrO_2 group were considered as the control/based samples (without adding reinforcing powder). The other six groups contain ZrO_2 or diopside particles composited with the glass ionomer powder. Figure 1 presents a schematic illustration of the fabrication process of the glass ionomer cement, including the filler materials, mixing with the polyacrylic acid, and final cement preparation.

Figure 1-The schematic illustration of the fabrication method of glass inomer cement.

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Table 2- Coding are referred to in the context of cement composites and reinforcements containing diopside and ZrO_2.

Code Sample	Ca-Cement	2Dio-Ca-Cement	4Dio-Ca-Cement	6Dio-Ca-Cement	$8ZrO_2$-Ca-Cement	$10ZrO_2$-Ca-Cemet	$12ZrO_2$-Ca-Cemet
wt.% of filler	0	2	4	6	8	10	12

2-6- Characterization

The properties of as quenched glass powders were examined using X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis to assess compositional changes. The diffraction data were collected using a Cu-Kα radiated diffractometer (D8 Advance, Bruker Kanagawa Japan) operating at 20 kV and 10 mA . Additionally, scanning electron microscopy (SEM) and simultaneous thermal analysis (STA) were employed for further evaluation. The powder-to-liquid ratio of 1.5 was utilized to prepare composite GIC composites. The setting time of the cement formulations was also measured using a Gillmore needle apparatus according to ISO 9917-1:2007 standards. For each composition, three specimens were tested and the average setting time was reported. Compressive strength was evaluated after 24 h of immersion in distilled water. According to ISO 99171:2007 guidelines, specimens prepared for compressive strength testing 6 mm in height and 4 mm in diameter. Also, the surface morphology of the zirconia-reinforced samples was examined using scanning electron microscopy (SEM). Moreover, samples intended for microhardness testing had dimensions of 6 mm in diameter and 2 mm in height. Vickers hardness measurement was done by a digital microhardness tester (Matsuzawa, MXT70, JAPAN) with an applied load of 100 grams for 10 seconds. The hardness value obtained for each sample is an average result of three different points on the surface.

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3- Results and Discussion

3-1- XRD results

Figure *2* (a) and (b) show the xrd patterns of the purchased zirconia and synthesized diopside powders, respectively.

The prominent peaks observed in this pattern are characteristic of the monoclinic phase of zirconia, which is its most stable polymorph at room temperature. The positions and relative intensities of these peaks are consistent with the JCPDS reference data for monoclinic ZrO_2 in the JCPDS Card (01-078-0091), confirming the phase purity and crystallinity of the as-received zirconia material. The XRD patterns of synthesized DIO exhibit a notable peak at $2\theta = 30^\circ$ and another significant peak at approximately 36° which is consistent with the characteristics peak of DIO reported in the JCPDS reference card (96-101-1048).

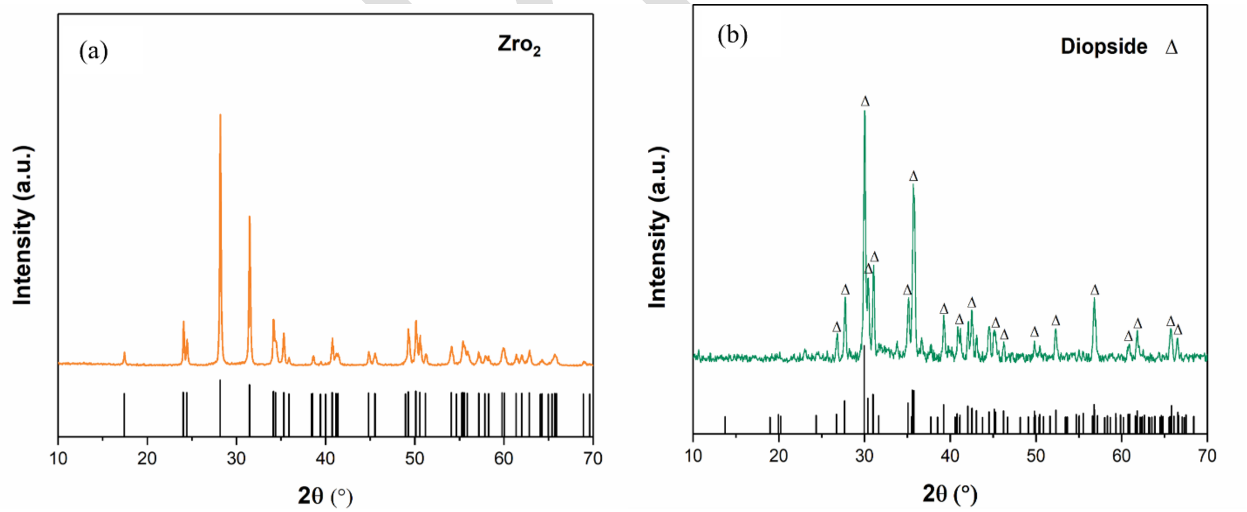

Figure 2- XRD patterns of (a) purchased zirconia (ZrO_2) and (b) synthesized diopside ($CaMgSi_2O_6$).

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3-2- Particle Size and Microstructure of Composite

Particle size plays a crucial role in determining the performance of composite materials, particularly in cement-based systems [39, 40]. The filler particles in most studies are smaller than 100 nm or in the micron range [16]. The frits and diopside were grinded for 3 h in the zirconia cup at 300-rpm in a planetary mill (pm 400,Retch,.Germany) The resulted powders were examined using the particle size analyzer (PSA). Figure *3*-a shows the SEM image of as-milled glass powders. PSA result is depicted in Figure *3*-b. The results revealed that the glass particles range within the 1-10 µm.

The dynamic light scattering (DLS) method was employed to determine the median size of the synthesized diopside post-milling and sieving and the as-milled zirconia particles which was in the range of approximately 220 and 200 nm, respectively (Figure *3*-c and d).

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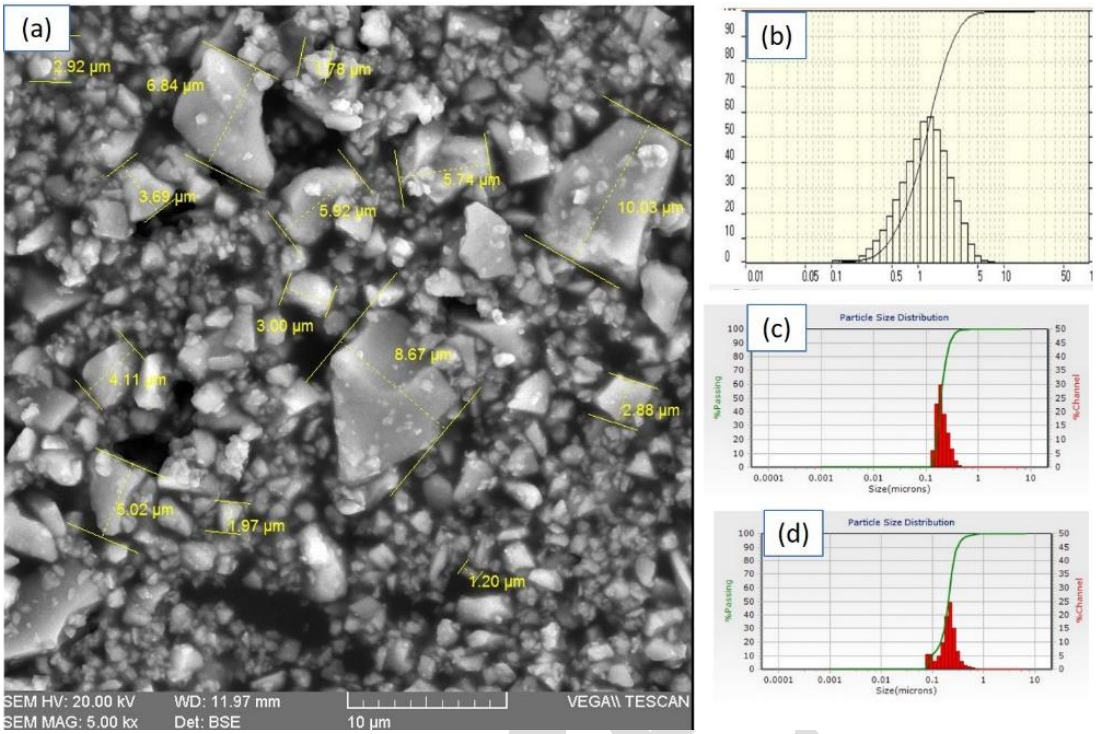

Figure 3-(a) SEM image of melted and milled glass particles (b) PSA analysis of synthesized glass particles (c) DLS analysis of synthesized diopside particles (d) DLS analysis of purchased zirconia powders

Beyond particle size, understanding the internal structure and chemical environment of the glass is critical for predicting its reactivity and performance in GICs. Calcium aluminosilicate (CAS) glasses contain both bridging oxygen (BO) and non-bridging oxygen (NBO) ions that define their structure [41, 42]. Studies indicates that fluoride-substituted oxygen tends to bond with modifiers in high-fluoride glasses [43]. Conversely, 19F and 29Si NMR analysis showed poor bonding between fluorine and silicon, increasing the likelihood of F-bonding with calcium and aluminum compared to Si-F bonding [44]. Additionally, the glass in this study exhibited a tendency toward amorphous-amorphous/crystalline phase separation, which may result in nanoscale heterogeneities or localized crystalline regions within the amorphous matrix [37].

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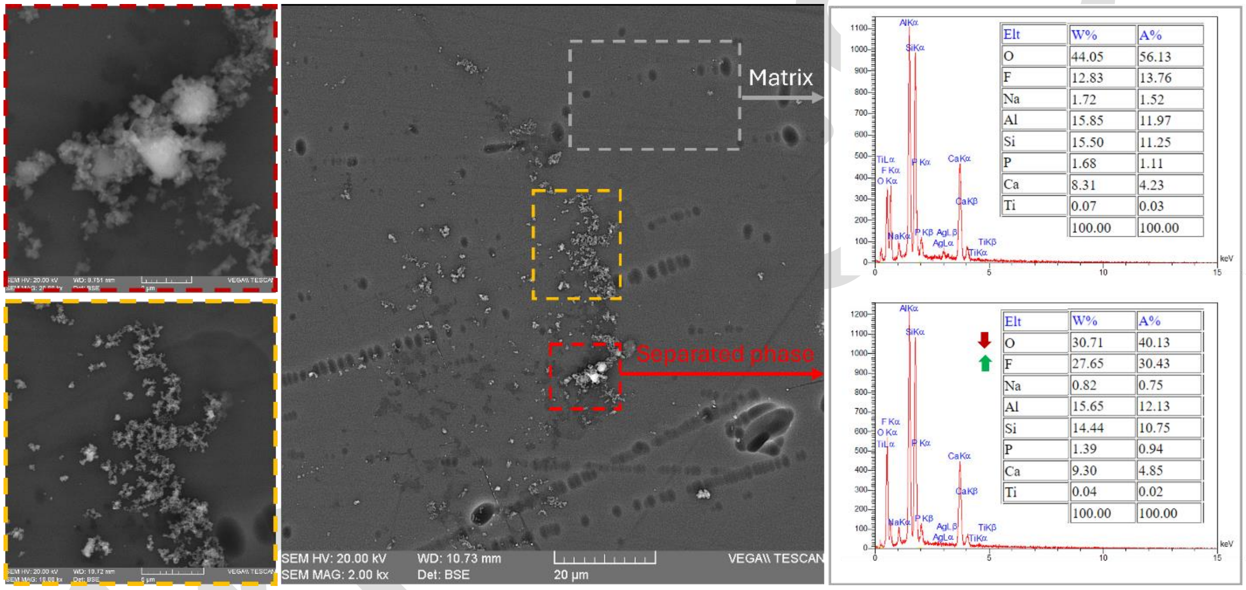
Figure 4 illustrated the SEM images and EDS analysis of etched firit glass surfaces which revealed limited formation of fluorine-rich crystalline zones on glass particle surfaces. Although the percentage of separated phases was not as high as indicated in the XRD analysis, the presence of these phases in the synthesized glass positively can affect the cement by reducing its setting time. In such a way, it improves acid hydrolysis and it has led to more reactivity of the glass powder with acid. This separation facilitating the availability of participating elements to cross-link with polymeric matrix during the setting stage of cement.



Elt	W%	A%
O	44.05	56.13
F	12.83	13.76
Na	1.72	1.52
Al	15.85	11.97
Si	15.50	11.25
P	1.68	1.11
Ca	8.31	4.23
Ti	0.07	0.03
	100.00	100.00

Elt	W%	A%
O	30.71	40.13
F	27.65	30.43
Na	0.82	0.75
Al	15.65	12.13
Si	14.44	10.75
P	1.39	0.94
Ca	9.30	4.85
Ti	0.04	0.02
	100.00	100.00

Figure 4-Examination of etched glass surfaces and observation of fluorine-rich isolated phases by SEM and EDX analysis.

3-3- Thermal behavior of the glass

Figure *5* illustrates the thermal behavior of the glass powder. The glass transition temperature (T_g) is observed at 510°C, followed by a broad exothermic peak around 850°C. Heating the glass to 850°C for 15 min resulted in the formation of calcium anorthite crystalline phases, as confirmed by XRD analysis (Figure *5*-b) [42]. It is important to distinguish between glasses with a stoichiometric anorthite composition (amorphous) and crystalline anorthite ($CaAl_2Si_2O_8$), as their reactivity, particularly with organic acids in glass ionomer cements, differs significantly. However, it is pertinent to note that the overall chemical composition of our glass, when plotted on the relevant $CaO-Al_2O_3-SiO_2$ phase diagram, falls within the primary crystallization field of anorthite, which explains its formation upon thermal treatment. While literature suggests that glasses with a bulk anorthite composition may exhibit longer setting times in glass ionomer cements compared

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to gehlenite glass compositions, the specific impact of the observed anorthite crystallization on the reactivity of this particular glass requires further investigation [45].

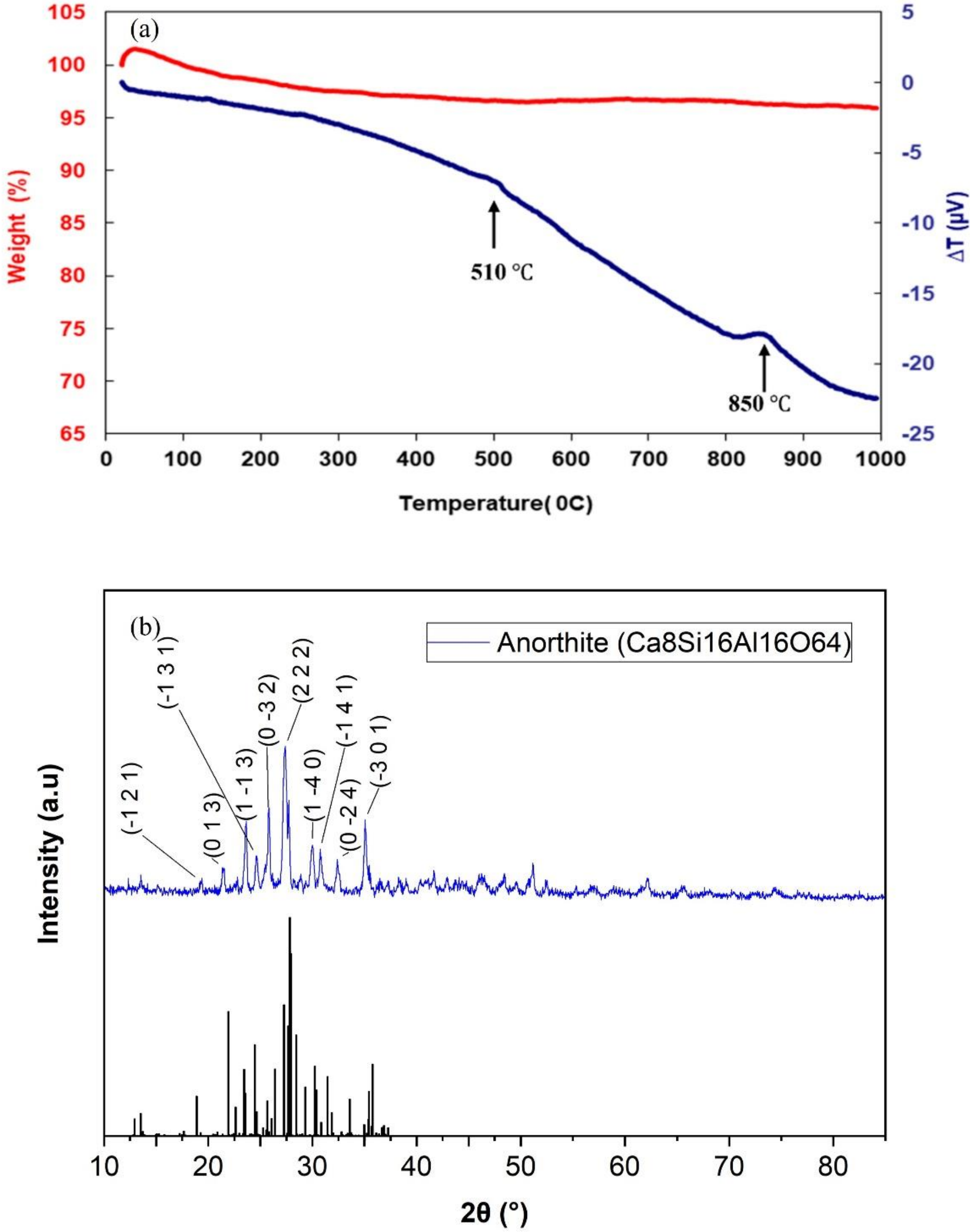

Figure 5- a) Differential thermal and thermogravimetric analysis curves of Ca-Glass, b) X-ray diffraction pattern of heat-treated glass at 850°C for 15 minutes.

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3-4- The setting time of GICs

The setting time of glass ionomer cements (GICs) is a crucial clinical property and influencing workability. In this study, the base cement (control) exhibited a setting time of 6.5 min. Interestingly, the addition of both zirconia and diopside fillers led to an increase in setting time, albeit to varying degrees.

For zirconia-modified cements, the setting time slightly increased to 7.4, 7.6, and 7.9 min with the addition of 8, 10, and 12 wt.% zirconia, respectively. This observed increase is primarily attributed to the barrier effect of the zirconia particles. Zirconia, being chemically stable and relatively inert in the acidic GIC environment, physically obstructs the direct contact between the active glass particles and the polyacrylic acid solution. This impedes the initial acid-base reaction, which is fundamental for ion release and the subsequent cross-linking process, thereby prolonging the overall setting time.

In contrast, diopside additions resulted in more pronounced increases in setting time, reaching 8.3, 8.7, and 9.1 minutes for 2, 4, and 6 wt.% additions, respectively. Similar to zirconia, diopside particles can also exert a physical barrier effect, hindering the direct interaction between the glass and polyacid. However, diopside's impact on setting time is further exacerbated by its basic nature. Beyond the physical impedance, the basicity of diopside leads to a partial neutralization of the polyacrylic acid, which is essential for dissolving the glass and initiating ion release. This premature neutralization directly interferes with the acid-base reaction kinetics, limiting the optimal release of cross-linking ions (like Al^{3+} and Ca^{2+}) from the main glass powder. Consequently, the formation of the robust 3D polyacrylate network is delayed, resulting in a more significant increase in the setting time compared to zirconia.

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The distinct influences of zirconia and diopside on setting time highlight the complex interplay between filler particle properties (inertness vs. reactivity, physical vs. chemical effects) and the intricate acid-base setting mechanism of GICs.

3-5- The mechanical properties of GIC

According to ISO 9917-1:2007, the compressive strength (CS) and microhardness (HV) tests are recognized as suitable criteria for evaluating the strength of GICs. Compressive strength is defined as the maximum stress a material can withstand without failing. This measure is widely utilized as a method for assessing the strength of dental cement materials, including GICs. In this study, the mechanical properties of composite cement according to Table 2 with the addition of 2, 4 and 6 wt.% diopside powder, as well as composite cement with 8, 10, and 12 wt.% zirconia powder, were examined. Compressive strength and hardness were measured from the optimal percentages of composites with zirconia and diopside.

The average compressive strength results of various cement groups are presented in Figure 6, measured after 24 h of setting. The control sample demonstrated a baseline strength of 44.08 MPa. Among the zirconia-based composites, the 8ZrO_2-Ca-Cement formulation achieved the highest compressive strength of 65.9 MPa, representing a 49% improvement over the control sample. Notably, all zirconia-containing glass ionomer cements GICs exhibited superior strength compared to the control group. In contrast, the diopside composites showed varying strengths ranging from 14.5 to 44.02 MPa across different concentrations (2, 4, and 6 wt. %). Within this group, the 2DIO-Ca-Cement formulation achieved the highest compressive strength. However, unlike zirconia, the addition of diopside did not demonstrate a positive effect on composite strength.

While the absolute compressive strengths obtained are lower than typical commercial GICs (e.g., Fuji II, which can exceed 168 MPa at 24 h), this is primarily attributed to the properties of our

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synthesized polyacrylic acid (PAA) polymer. An experiment combining commercial Fuji II glass powder with our PAA yielded approximately 75 MPa at 24 h, suggesting that the lower molecular weight of our PAA, compared to proprietary commercial polymers, significantly impacts the overall cement strength. Despite this, the observed trends and relative improvements with zirconia and diopside additions remain valid within our experimental system, guiding future optimization towards higher molecular weight polymer synthesis.

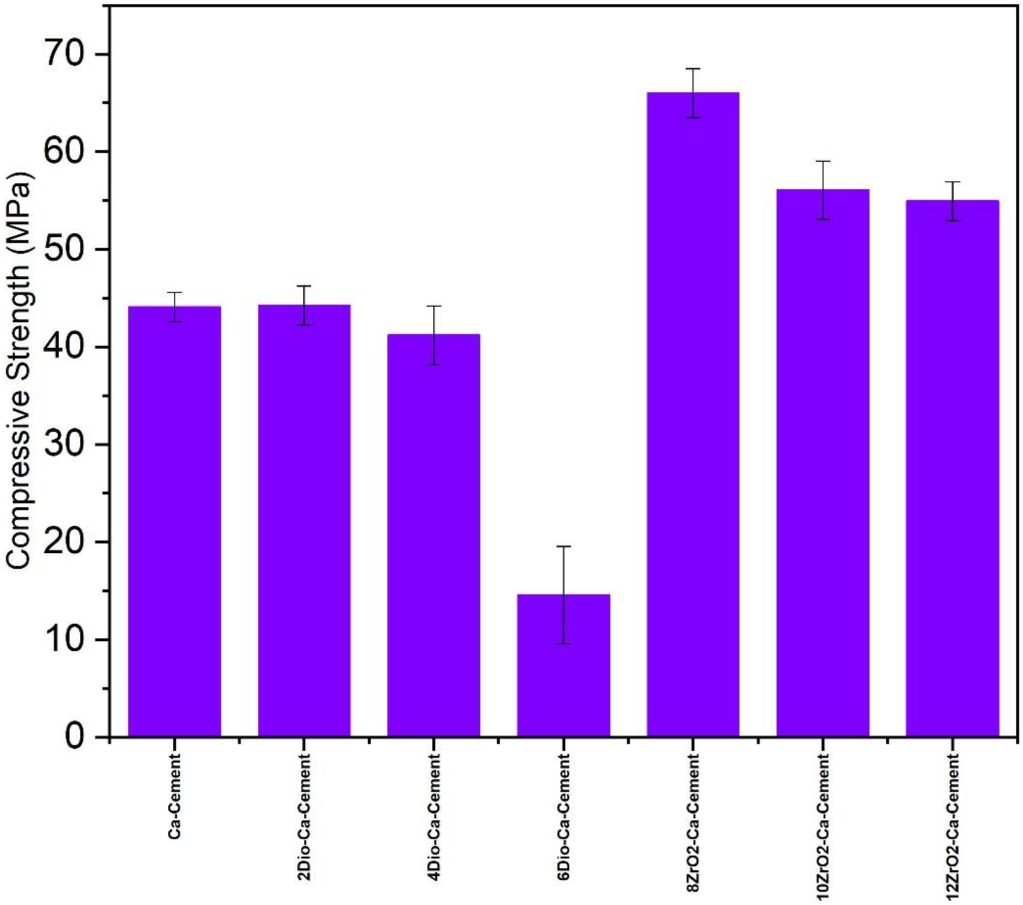

Figure 6- The compressive strength of cement samples containing diopside and zirconia measured after immersing in distilled water for 1 day.

Previous research has demonstrated that incorporating zirconia nanoparticles, particularly those less than 100 nm, improves the mechanical properties of GICs [46, 47]. Studies have conclusively

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established that most ceramic nanoparticles contribute to enhanced strength characteristics primarily by reducing the porosity and inducing crack deflection mechanisms [48, 49]. Conversely, certain investigations have revealed limitations associated with the aggregation of nanometer-scale materials, resulting in diminished control over particle size distribution and consequently resulting the detrimental effect of zirconia-based composites [47, 48]. Furthermore, there is a lack of experimental data examining the compressive strength attributes of submicron GICs incorporating zirconia powder. Some Studies has indicated that zirconia within the submicron (spanning 1 µm to 10 µm) can enhance the mechanical properties [47, 48]. However, other findings suggested that increasing the percentages of nano-micron zirconia may less positively affect the improvement of compressive strength characteristics [47]. This phenomenon can be attributed to various factors. Generally, higher percentages of the second phase tend to increase accumulation and clustering, often leading to increased porosity in the composite structure. Such porosity can serve as a nucleation site for crack formation under applied forces [48]. Furthermore, elevating the volume fraction of zirconia may extend the duration of the cement setting and facilitate the formation of insufficient cross-link bonds within its polymer chains. Diopside contains high levels of magnesium and calcium cations that can contribute to cement reactions and exhibits a more basic nature compared to both calcium-aluminosilicate glass powder and zirconia [26].

3-6- Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analysis of the composite materials reveals distinct variations in zirconia particle distribution. The 8ZrO_2-Ca-Cement formulation demonstrates optimal zirconia particle dispersion across the surface. However, SEM examination of specimens containing 10 and 12 weight percent zirconia reveals evidence of particle agglomeration on the surface (Figures 7c and 7d). As illustrated in Figure 7c, the formation of larger zirconia

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agglomerates creates potential crack initiation sites under compressive loading. Furthermore, as the zirconia content increases in the composite formulation, particle distribution becomes progressively compromised, leading to increased accumulation of zirconia particles.

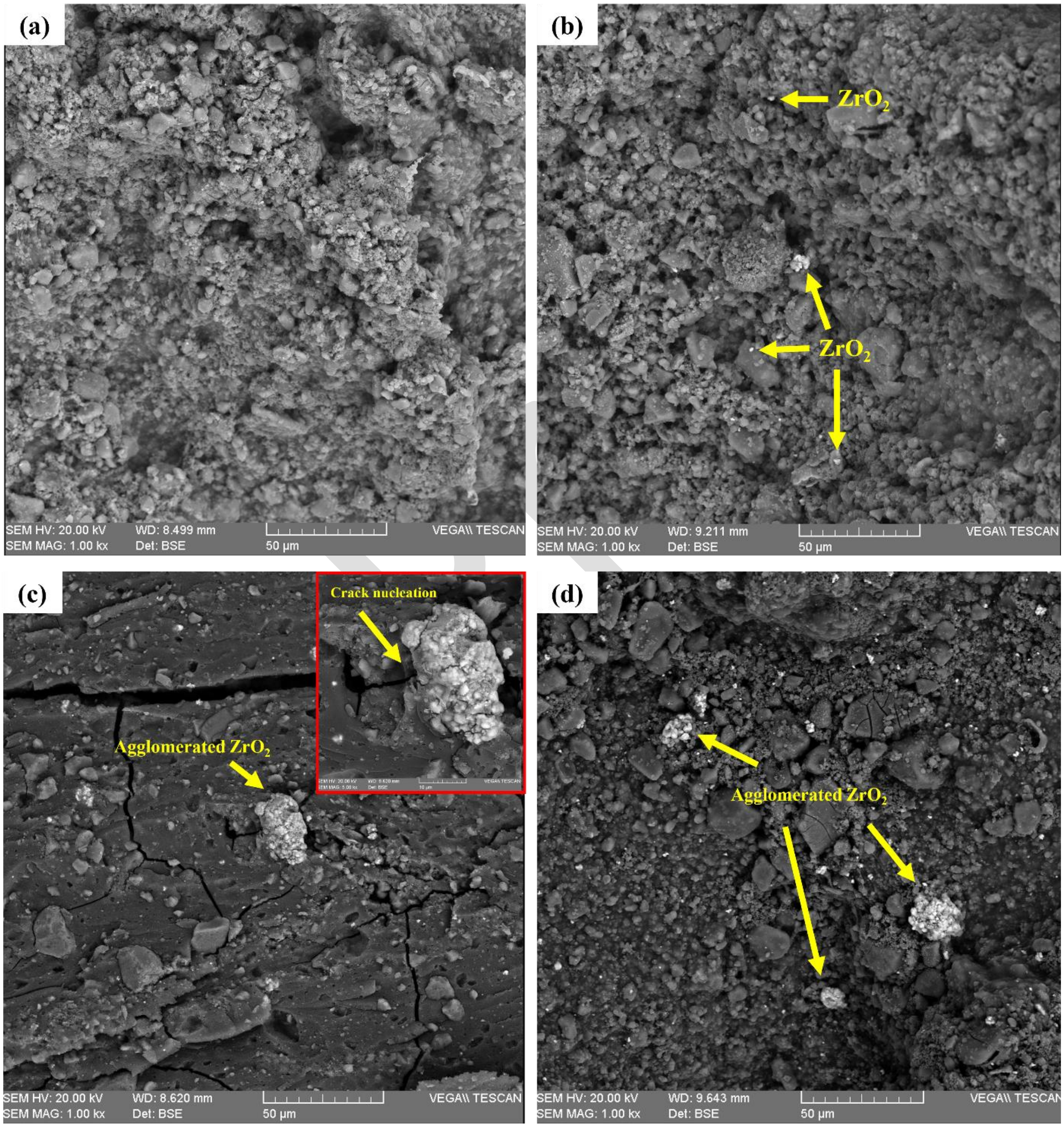

Figure 7- SEM image of composites : (a) Ca-Cement, (b) 8ZrO2-Ca-Cement, (c) 10ZrO2-Ca-Cement, (d) 12ZrO2-Ca-Cement,

3-7- FTIR results

The correlation between the intensity of symmetrical and asymmetrical cross-links formed and cement strength was studied via FTIR spectroscopy. The spectra of samples, specifically within the 1300-1800 cm^{-1} range, are presented in Figure 8. The symmetrical and asymmetrical cross-links formed arise from the interaction between aluminum and calcium ions with COO^- functional group during the setting reaction. Absorbtion bands of 1469 and 1619 cm^{-1} are associated with symmetric and asymmetric aluminum carboxylate compounds, respectively [25, 50]. In 4Dio-Ca-Cement (red), the reduced intensity of these aluminum carboxylate bands, compared to Ca-Cement (green) and $10ZrO_2$-Ca-Cement (black), indicates a diminished formation of aluminum carboxylate cross-links. Moreover, calcium carboxylate absorption symmetric and asymmetric bands are 1415 and 1574 cm^{-1}[25]. Furthermore, the lower intensity of symmetric and asymmetric Ca- COO^- bonds in 4Dio-Ca-Cement, compared to Ca-Cement, indicates a lower degree of cross-linking within the cement matrix [38, 50, 51].

The overall diminished salt-carboxylate network (COO^- Ca^{2+} and COO^- Al^{+3}) in diopside-modified cement is a direct consequence of diopside's basicity. This basic nature interferes with the setting reaction by partially neutralizing the polyacid and thus limiting the critical ion release from the glass powder, hindering the complete formation of the robust 3D polymer-salt network. In contrast, zirconia's neutral nature allows for proper network development. Diopside's rapid ion release also disrupts the glass-acid reaction, delaying setting and weakening initial cement strength [52].

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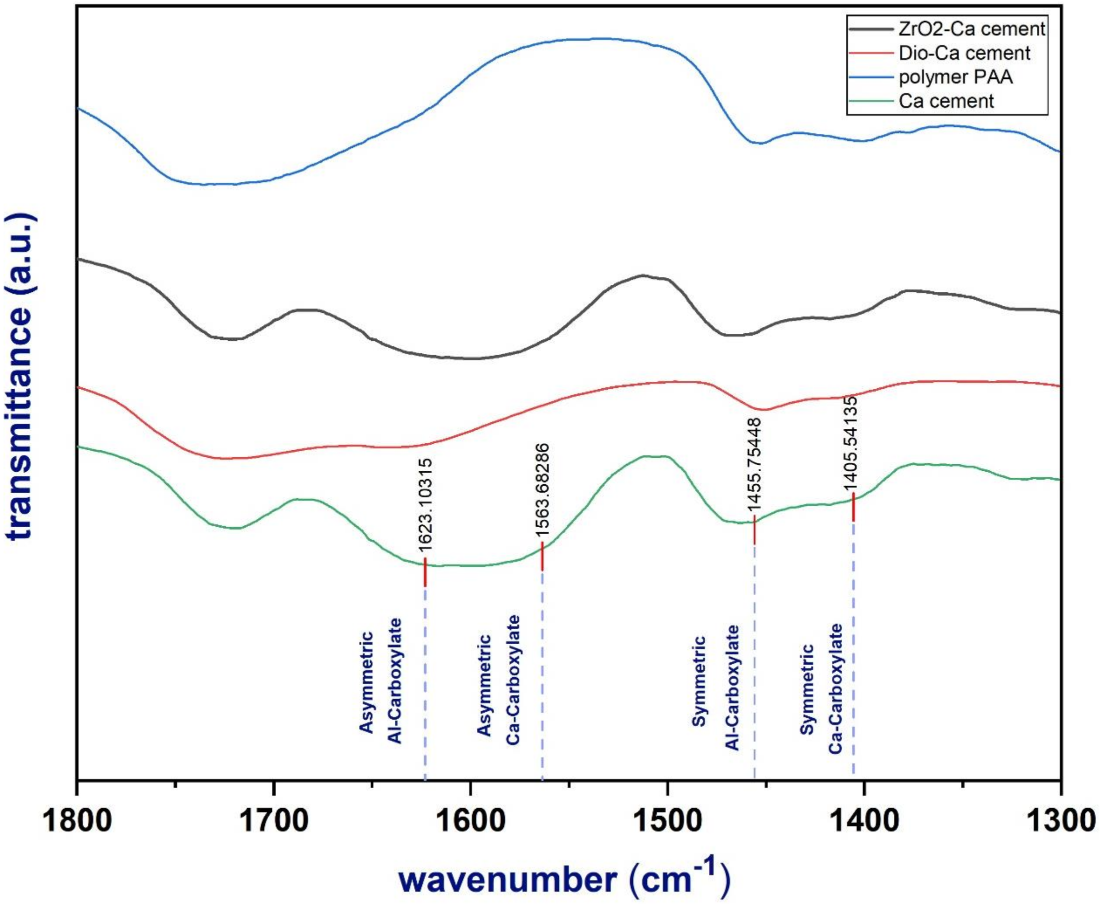

Figure 8-FTIR spectra of GICs containing: PAA polymer (blue), Ca-Cement (green), 4Dio-Ca-Cement (red), and 10ZrO_2-Ca-Cement (black)

3-8- The microhardness of the cement

The wear resistance of dental restorative materials in the actual oral environment can be assessed using the microhardness test as a criterion. The microhardness data of GIC samples are illustrated in Figure 9 which were measured according to the ISO 9917-1:2007 standard. In ZrO_2-Ca-cements, a significant increase in hardness can bee seen compared to Ca-cements. This is likely due to the inherently harder nature of zirconia particles than glass particles, suggesting that a higher concentration of zirconia results in a harder material.

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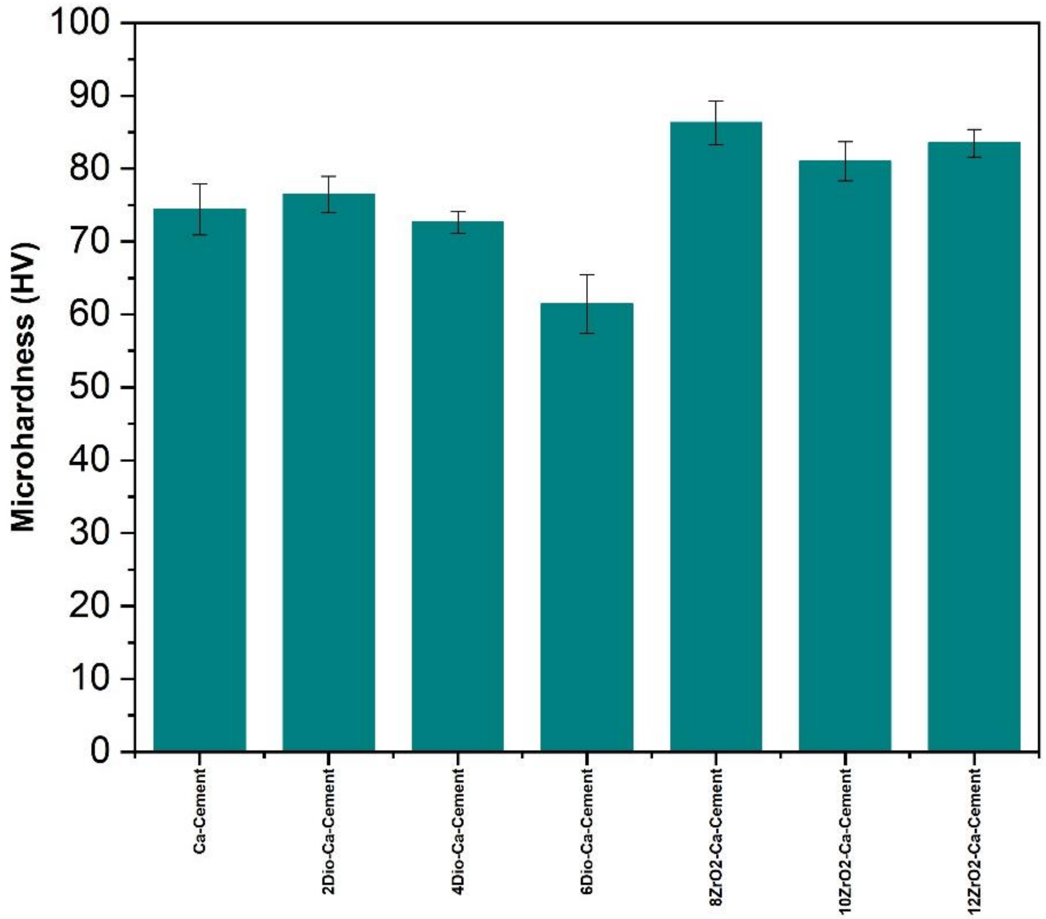

Figure 9. Microhardness measurements of GIC reinforced with varying concentrations of zirconia and diopside nanoparticles.

Also, adding 2% diopside to the glass ionomer resulted in a slight increase in hardness than Ca-cement. However, a decrease in hardness was observed upon further increasing the amount of Diopside and zirconia in the composite composition of the glass ionomer. On the other hand, it is believed that the reduction in microhardness due to an excess of diopside particles suggests insufficient bond between the PAA polymer and glass particles. This phenomenon can be attributed to the number of carboxylic acid groups available for bonding with glass particles. As the percentage of diopside particles increases, cracks around these nanoparticles become more prevalent. Consequently, the number of cracks in the interface also increases, resulting in a significant drop in microhardness.

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4-Conclusions

This study aimed to develop GICs with enhanced mechanical properties for restorative dental applications. To achieve this, the effects of incorporating different percentages of zirconia and diopside nanoparticles (refer to Table 2) into the cement matrix were investigated. The results demonstrated that zirconia significantly improved the compressive strength of the GIC and 8 wt.% zirconia yielded a 46% increase in strength. This enhancement can be attributed to the more acidic nature of zirconia compare to glass powder, which facilitated stronger interfacial bonding within the cement matrix. In contrast, diopside, with its more basic nature, did not significantly improve the mechanical properties. Also, less bonds between the PAA and the Dio-Ca glass than ZrO_2-Ca glass because of their basic nature, resulted in weaker microhardness. Regarding setting time, both zirconia and diopside additions resulted in a longer setting time for the GICs. Zirconia primarily acted as a physical barrier, slightly impeding the acid-base reaction. Diopside, however, caused a more pronounced increase in setting time due to its basicity, which interfered with the acid-base reaction kinetics by neutralizing the acid and limiting ion release, thereby hindering optimal network formation. These findings highlight the crucial role of the acid-base properties of additives in determining the overall mechanical performance of GICs. Further research is needed to optimize the selection and incorporation of reinforcing agents for improving clinical outcomes.

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