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Enhancing Properties of Metakaolin-Based Geopolymers: The Effect of Zirconia and Silica Nanosphere Additions

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Geopolymers are known for its high compressive but low tensile strength due to its brittle nature, which restricts the use of geopolymers as structural material. It is important to enhance their mechanical performance by incorporating reinforcing materials. This research examines the contribution of silica nanospheres and zirconia to enhance the tensile strength of geopolymer composites utilizing metakaolin. Geopolymers were prepared from an 8M NaOH and sodium silicate activator, which was prepared for 24 hours prior to mixing in a ratio of 2:1. Confirmation of the amorphous silica presence, monoclinic and tetragonal zirconia, and crystalline phases in metakaolin including quartz, mullite, and hematite was verified using X-ray diffraction (XRD) analysis. The scanning electron microscope (SEM) showed that both silica nanospheres and zirconia resulted in a more densely packed microcomposite material with less porosity. Diametral tensile strength (DTS) at 28 days demonstrated that integrating 80% silica nanospheres increased tensile strength by 15.2%, while the mixture of 60% zirconia and 20% silica nanospheres resulted in a 61.2% strength enhancement compared with the control (from 2.24 MPa to 3.61 MPa). These improvements showed that nanomaterials such as silica can enhance the densification of the matrix while zirconia contributes structural reinforcement for improved mechanical properties. The findings here are consistent with earlier work that demonstrated the synergistic effects of silica nanospheres and zirconia to improve geopolymers performance. Findings from this study further demonstrates modified geopolymers can be used in applications requiring high mechanical strength but would require additional investigation to determine its durability and thermal properties to use them in structural and functional applications.

Keywords: geopolymer; zirconia; silica nanospheres; sol-gel; diametral tensile strength; morphology.

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Introduction

Geopolymers are advanced inorganic polymers that have received great interest recently due to their durable mechanical properties [1, 2] and low greenhouses gas emissions [3] which makes them a suitable substitute for cement. These materials are synthesized with the help of alkaline solutions on raw materials rich in aluminosilicate like fly ash, slag, metakaolin etc. Metakaolin, a calcined form of kaolinite clay, is one of them, which has a good silica and alumina content that is available, reactive and abundantly used for geopolymer production [4]. The compressive strength and thermal stability of Metakaolin

based geopolymers can be used for various construction applications. Despite these benefits, metakaolin-based geopolymers face several issues including brittleness [5], shrinkage [6], and a lack of aesthetics. Such issues can affect the performance of the material and limit its practical use for certain application. To tackle these issues, various fillers and additives have been used by researchers to enhance the mechanical and physical properties of geopolymers [7]. Nanoparticles are one of the most effective additives because of their high surface area [8], smaller size, and unique structural properties can significantly improve the material's properties [9]. Zirconia (ZrO₂) and silica (SiO₂) nanosphere are expected to enhance the strength, toughness, and thermal stability

of the geopolymer. Zirconia possesses high hardness and wear resistance [10]. Silica nanospheres have high surface reactivity [11], which improves the bonding of the matrix to the fillers and makes the composite durable. Adding these nanomaterials to geopolymer matrices could reduce the inherent weakness of the metakaolin-based geopolymers (brittleness and shrinkage), while also improving their mechanical performance. Most studies show improved compressive strength, flexural strength, and crack resistance. For example, the study of Saukani et al. [12] show that zirconia increases the compressive strength of metakaolin-based geopolymer by 23%. Additionally, zirconium oxide has been reported to retard the crack initiation and propagation in geopolymer mortar composite [13]. Moreover, the inclusion of nanosilica increased the flexural strength and fracture toughness of fly ash-based geopolymer was increased by 82%, reported by the study of Rahmawati et al. [14]. Despite these, few studies show the effects of zirconia and silica nanosphere on the diametral tensile strength of metakaolin-based geopolymer even with these advances.

This study aims to determine the impact of zirconia and silica nanospheres on diametral tensile strength of metakaolin-based geopolymer. The morphology of geopolymer matrix modified nanoparticles were analyzed by Scanning Electron Microscopy (SEM). Through the improved understanding of zirconia and silica nanospheres' effects, the research can help develop future generation geopolymer-based materials that will take the best from the standard geopolymers and their next-generation composites. Ultimately, these fillers may help create far more sustainable and cost-effective materials for a multitude of advanced science and engineering uses.

I. Materials

The materials used for sol-gel methods and geopolymer synthesis, namely Calcium Chloride (CaCl_2), ethanol ($\text{C}_2\text{H}_5\text{OH}$), acetic acid (CH_3COOH), tetraethylorthosilicate (TEOS), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), deionized water, and chitosan were obtained from Brataco Chemical Bandung, West Java, Indonesia. The Kaolin were obtained from Batujajar, West Java, Indonesia. The material was calcined at 700°C to produce metakaolin, based on previous study [15]. Table 1 shows the chemical composition of metakaolin, using X-Ray Fluorescence (XRF) method.

Table 1.
Chemical composition of Metakaolin.

Material	Chemical composition			
	SiO_2	Al_2O_3	CaO	Na_2O
Metakaolin	65.00	33.00	0.08	0.06

II. Methods

2.1. Synthesis of zirconia

Several steps were involved in the synthesis of zirconia nanoparticles. First, a stirred mixture of

4.66 grams of ZrCl_4 precursor and 200 mL of de-ionized water in a magnet stirrer for 15 minutes produced a 0.1 M ZrCl_4 solution. To stabilize this solution, 0.234 grams of CaCl_2 , a precursor to the synthesis of the silica nanospheres with a purpose of the provision of calcium ion source for gelation, was added and stirred one more time for 15 minutes until the solution was homogenous. The mixture was aged and dried at 120°C in the oven for 24 hours, which helped to evaporate the solvent and form xerogel. The xerogel was ground to fine powder using pestle and mortar. The sample was placed in a combustion boat and calcined in a furnace from room temperature to 900°C for 2 hours to form fine powders. The temperature was reduced after the calcination process. The solid mass obtained after calcination was grinded again using mortar and pestle. 50mL of ethanol, used as a solvent for making the suspension of nanoparticles which helped to disperse the materials, was added to the powder and ultrasonic homogenizer was used at 80 amplitude for 30 minutes to produce nanoparticles. Finally, the sample was dried in the oven until all the liquid evaporated, and the powder was ground again to obtain the final zirconia nanoparticle product.

2.2. Synthesis of silica nanosphere

The synthesis of silica nanospheres were also involving the addition of chitosan, a biopolymer that is derived from chitin and is used to enhance the mechanical and stability of the composite. Initially, a beaker was taken, and 98 mL de-ionized water was added. Later, 2 mL CH_3COOH , serves as a catalyst to regulate the pH during the synthesis process, was added and the resulting mixture stirred for five minutes using a magnetic stirrer. Afterwards, 2 grams of chitosan was added to the solvent and stirred for 2 hours until the solution became turbid. In another beaker, 200 mL $\text{C}_2\text{H}_5\text{OH}$, 20 mL DM aqua and 4 mL NH_3 to adjust pH leading to the formation of nanospheres and control of the sol-gel process were mixed and stirred for 10 minutes. After that, the solution was added with 12 mL of TEOS as the silica precursor and stirred for 5 minutes more. Later, 1 mL of 2% chitosan solution was added to the mixture, which was stirred for 90 minutes. Once all the water had evaporated, the solution was dried at 120°C to leave a dry silica precipitate. The dried precipitate was ground to yield silica powder using mortar and pestle. The powder is put into a combustion boat and calcinated in the furnace from room temperature to 900°C for 2 hours. The temperature was brought down after 2 hours. When cooled, the sample was taken out of the furnace and ground again using the mortar and pestle to achieve a smooth mixture. The heated silica sample was mixed with 50 mL of ethanol, sonicated at 80-amplitude for thirty minutes to yield nano-sized particles. At last, the sample was dried in an oven until free of liquid, and after grinding, silica nanosphere powder was obtained.

2.3. Synthesis of geopolymer

The preparation of alkali activator solution that contains 8M NaOH and Na_2SiO_3 in a ratio of 2:1 is the first step in the geopolymer synthesis process. Both chemicals were mixed and sealed for 24 hours before using to ensure complete dissolution, which adapted from

previous study [16]. The mixture of metakaolin, alkali activator, zirconia, and silica nanosphere were conformed to the proportions given in Table 2. Then, the geopolymer paste was cast into cylindrical molds of 6 mm diameter and 3 mm height. The geopolymer were kept at 80°C for 20 hours for curing. The hardened samples were removed from the molds were prepared for mechanical and structural testing.

Table 2.
Composition of Geopolymer Mixtures with Varying Amounts of Zirconia and Silica Nanospheres.

Group	MK (g)	Zirconia (g)	SiO ₂ (g)	NaOH (g)	Na ₂ SiO ₃ (g)
I	1.5	0	0	0.429	0.214
II	0.3	0	1.2	0.952	0.476
III	0.3	0.9	0.3	0.569	0.284

III. Mechanical properties

A diametral tensile strength test was performed at 28 days using the universal testing machine (Shimadzu Autograph AGS-5KNX). A maximum load of 1 kN and a crosshead speed of 1.0 mm/min were used in the test. The specimens were tested this way to obtain their tensile strength (or vertical separation during compression). The diametral tensile strength (DTS) of the geopolymer specimens was calculated using the following equation (1):

$$DTS = \frac{2P}{\pi Dt} \quad (1)$$

where P = maximum applied load (N); D = diameter of the specimen (mm); and t = thickness of the specimen (mm). This formula is derived from the Brazilian test method, which evaluates the tensile strength of brittle materials under compressive loading.

IV. Characterization of materials

The metakaolin, zirconia, and silica nanosphere were characterized using X-Ray Diffraction (Bruker D8 Advance). The analysis was performed with scanning angle from 10° to 80° (2θ) at a rate of 2.5°/min over a total acquisition time of 30 min. The morphology of both all raw materials mentioned, and the resulting geopolymers was evaluated by SEM (Hitachi SU3500). SEM observations were performed in high-vacuum mode at a 15 mm working distance, and images were captured at different magnifications to examine the change particle size of silica nanoparticles and morphological of modified geopolymer.

V. Results and discussions

5.1. XRD analysis of raw materials

Figure 1, Figure 2, and Figure 3 show the XRD diffractogram of silica nanospheres, zirconia, and metakaolin, respectively. The XRD diffractograms show the various crystalline phases and structural characteristics of the created materials. The diffractogram patterns were analyzed to validate the successful formation of silica nanospheres and zirconia, in addition to validating the minerals present in metakaolin.

Figure 1 presents a typical diffractogram of amorphous silica which displays a broad humps in the 2θ region of 20° to 35°, which confirms the disordered atomic arrangement and is representative of amorphous silica [17]. The absence of sharp crystalline peaks also suggests that the synthesized material indeed has a non-crystalline state, and there was no substantial degree of crystallinity after synthesis [18]. The broadening observed in the diffractogram may have also originated from the small particle size, which produces wider diffraction bands as it belongs to the porcelain effect which become dominant at smaller particle sizes. High purity of the synthesized silica is evidenced by the absence of additional phase peaks

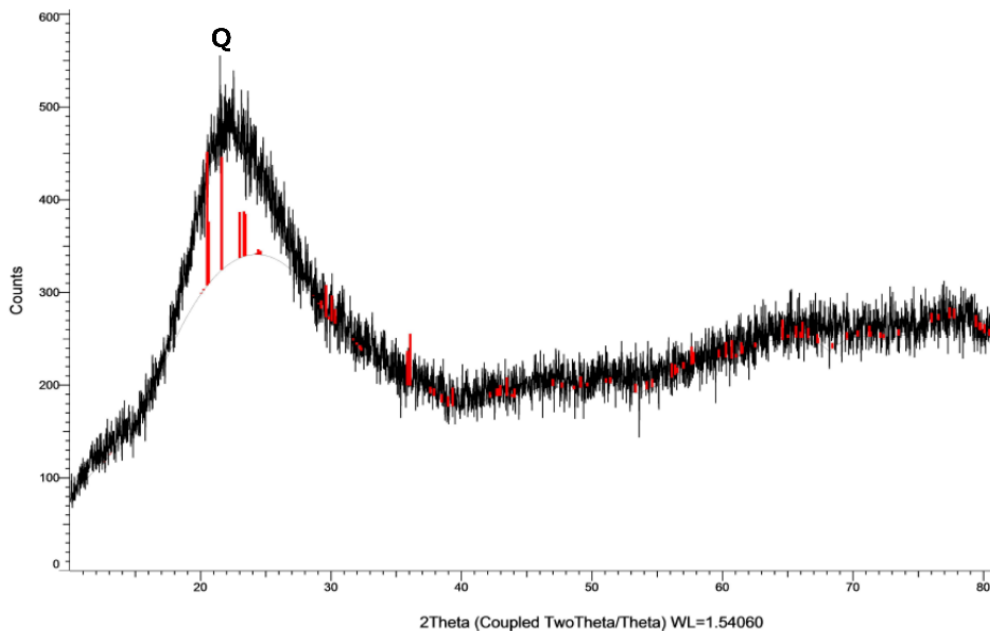


Fig. 1. Diffractogram of silica nanosphere from XRD characterization. Note: Q=Quartz (SiO₂).

indicating that the synthesized silica does not contain unreacted precursors or impurities of the final product [19]. Overall, the results presented suggest that the sol-gel method produced high purity silica, which is suitable for further applications in geopolymer composites.

The diffractogram of zirconia (Figure 2) exhibited both monoclinic and tetragonal phases. Most of the diffraction peaks belonged to the monoclinic phase, meaning the zirconia synthesized mostly crystallized in that structure. This agrees with its phase stability at room temperature where monoclinic zirconia is the most thermodynamically stable phase [20]. However, there were three distinct peaks relating to the tetragonal phase, which support that some zirconia was partially stabilized in its higher temperature phase [21].

Finding both phases could come from the effects of calcining, which induces transformation of the phase and stabilizes the tetragonal phase only partially and not as a single phase. Stabilization of the tetragonal phase would require a stabilizer agent like yttria [21] or calcia [22]. The mixed-phase behavior of zirconia can influence the

mechanical properties due to the transformation toughening mechanism of the tetragonal phase when under stress conditions and enhanced fracture resistance [23].

According to the XRD diffractogram of metakaolin (Figure 3), quartz, mullite, and hematite are the primary detected crystalline phases. The strong and sharp peaks of the quartz signal the presence of a largely intact or recrystallized silica-rich phase of the original kaolinite mineral during the thermal activation process [24]. The presence of mullite indicates that some decomposition and structural reorganization of kaolinite has occurred, which is anticipated during the thermal activation of kaolin above about 500°C [25]. Mullite is an important phase of metakaolin, as increased thermal stability and mechanical strength in geopolymer utilizes the influence of mullite phase [26]. Hematite is also detected, indicating the oxidation of contained iron impurities during calcination, which can control the color and pozzolanic reactivity of metakaolin [27]. Metakaolin contains both crystalline and amorphous phases, both of which combine to produce the

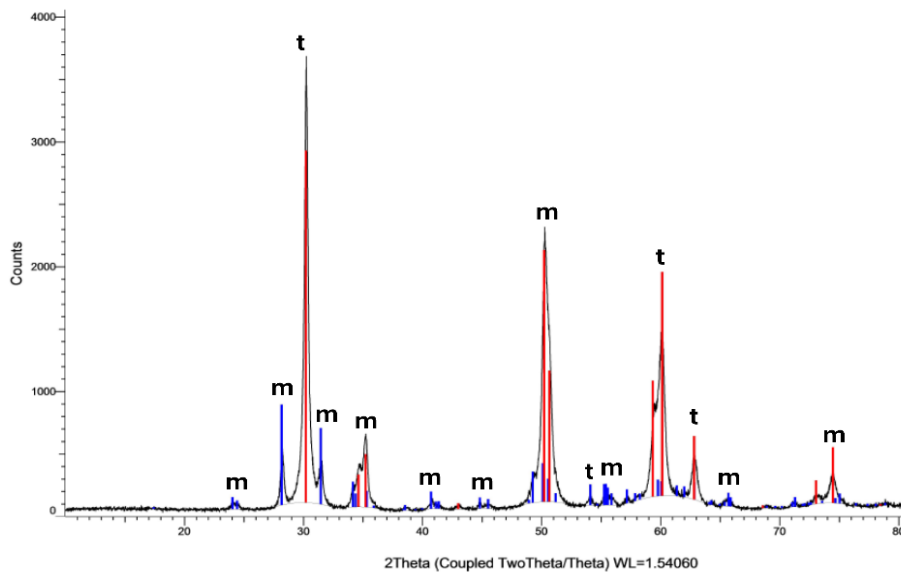


Fig. 2. Diffractogram of zirconia from XRD characterization. Note: m=monoclinic zirconia ($m\text{-ZrO}_2$); t=tetragonal zirconia ($t\text{-ZrO}_2$).

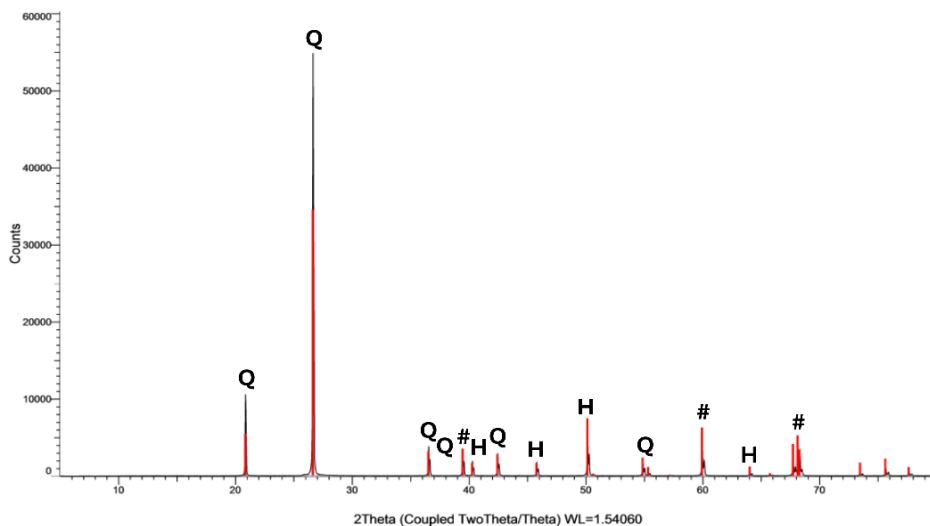


Fig. 3. Diffractogram of metakaolin from XRD characterization. Note: Q=Quartz (SiO_2); #=Mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$); H=Hematite (Fe_2O_3).

desired geopolymerization since amorphous aluminosilicate fraction provides the needed reactive phase for alkali activation.

5.2. Diametral tensile strength analysis

The diametral tensile strength of geopolymer composites with varying proportions of metakaolin, zirconia, silica nanospheres and alkali activator is shown in Figure 4. The results depict the effect of compositions on the mechanical characteristics of the geopolymer matrix in terms of diametral tensile strength, and the interaction of different proportions of filler and activator on tensile strength.

The diametral tensile strength (DTS) results back up the strengthening effects of silica nanospheres and zirconia in metakaolin-based geopolymer composites. Group I (control), which had metakaolin only performed at 2.24 MPa. In contrast, Group II increased the tensile strength to 2.58 MPa by incorporating 80% silica nanospheres and 20% metakaolin. This increase may indicate silica nanospheres improve particle packing and therefore reduced the porosity of the denser mixture and ultimately improved mechanical performance [28]. This has also been shown in the literature that silica nanoparticles improve geopolymers compressive and tensile strengths as it refines the microstructure and reduced defect within the geopolymer matrix [29]. In Group III that included 60% zirconia, 20% silica nanospheres, and 20% metakaolin, the tensile strength rose significantly to 3.61 MPa. The notable increase in tensile strength can be attributed to the toughening ability and reinforcement from zirconia, which has been shown to improve crack resistance and load-bearing ability in ceramic-based composites [30]. Prior work has shown that when included in a geopolymer matrix, zirconia improves mechanical properties due to its ability to act as a crack deflector and mechanically improve toughness and strength [31]. Therefore, combining zirconia and silica nanospheres results in an effective strengthening of the metakaolin-based geopolymer matrix, making it a viable

candidate for structural applications where enhanced tensile properties are necessary.

5.3. SEM analysis of silica nanosphere

The SEM image of the synthesized silica particles is displayed in Figure 5, and the particles' morphology is uniform and spherical in shape on a nanoscale. Each particle has a consistent shape, and the syntheses produced silica particles with a controlled morphology. Because of this distinct morphology, the nomenclature silica nanosphere is appropriate. The spherical morphology improves the properties available with the material, including better dispersion, lower agglomeration, and improved interfacial bonding in the geopolymer matrix.

The use of the phrase silica nanosphere is appropriate based on the morphological aspects shown in the Scanning Electron Microscopy (SEM) results. The SEM images show that spherical-shaped particles exist in the range of normatter, supporting the suitability of the descriptor "nanosphere." The spherical morphology is an important aspect of optimizing packing density, particle dispersion, and interfacial bonding within the geopolymer matrix. Moreover, the sol-gel synthesis method used in this study is already known for the synthesis of silica particles with controlled size and shape, typically yielding highly uniform and spherical nanoparticles [32]. Therefore, we assert that the SEM findings found in this study support the validity of using the term silica nanosphere in reference to the silica material synthesis presented in this study.

5.4. SEM analysis of geopolymer

The SEM images displayed in Figures 6, 7, and 8 show the variations in geopolymer composite microstructure that result from the different amounts of metakaolin, zirconia, silica nanospheres, and alkali activator used. These SEM images help demonstrate porosity, particle distribution, and the densification of each formulation and directly impact the mechanical properties of the geopolymer.

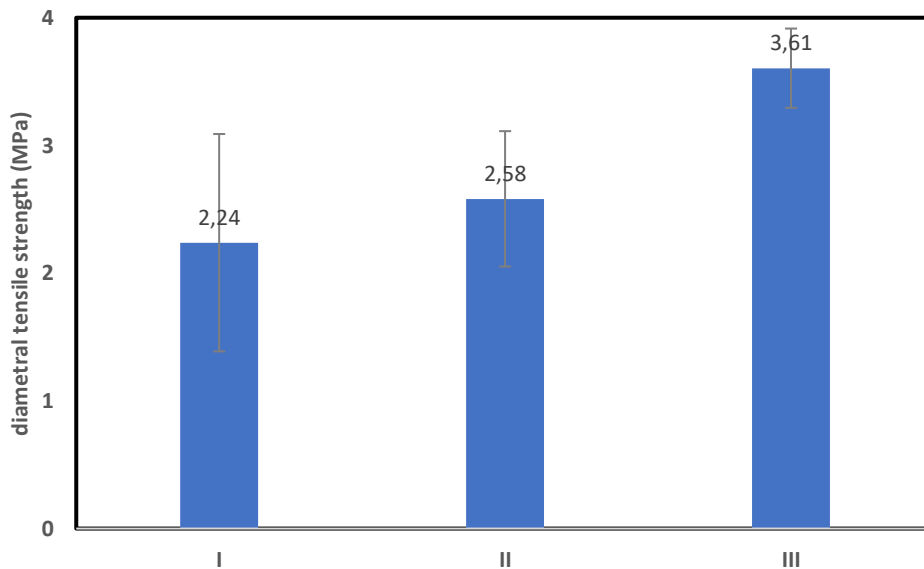


Fig. 4. Diametral tensile strength of geopolymer composites with varying percentages of metakaolin, zirconia, silica nanospheres, and alkali activator.

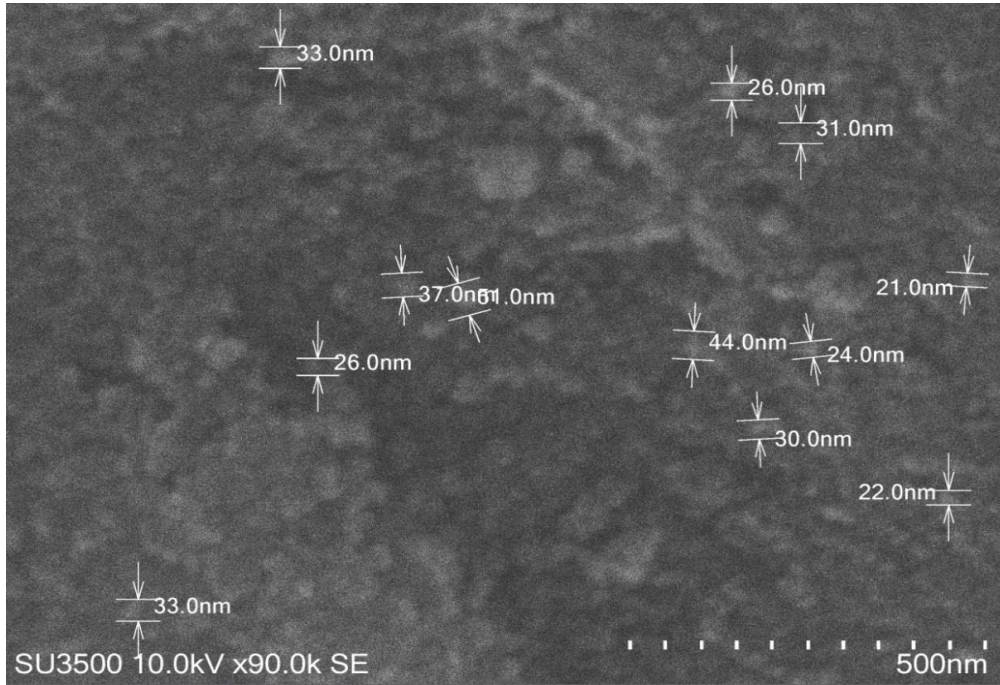


Fig. 5. A SEM image of synthesized silica nanospheres, showing uniform spherical morphology at the nanoscale, confirming the successful formation of silica nanoparticles (Magnification 90000×).

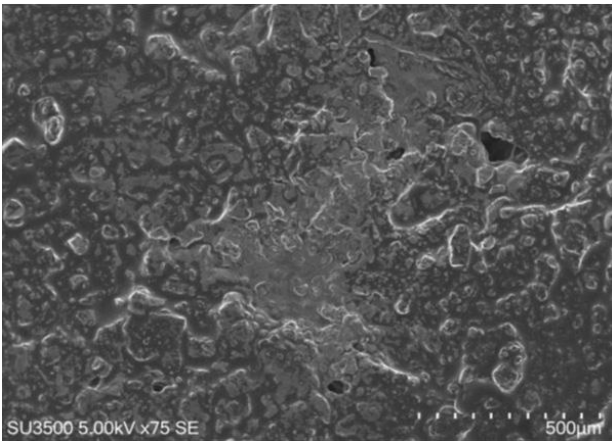


Fig. 6. A SEM image of Group I (Magnification 75×).

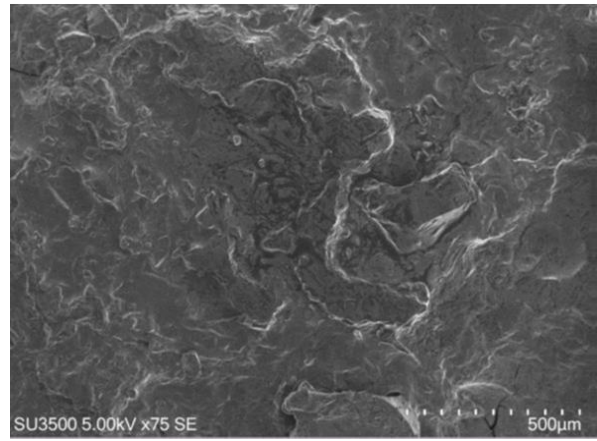


Fig. 7. A SEM image of Group II (Magnification 75×).

The SEM images obtained from the analysis conducted on Group I (100% metakaolin) show a rough and highly porous microstructure, exhibiting some cracks and overflowing, which are indicative of uncompleted geopolymerization and compromised mechanical properties. The presence of voids shows that the material is not densely packed but suggests the lower diametral tensile strength. This morphology is reasonable for geopolymers produced using only metakaolin, with no enhancing agent because the aluminosilicate network is formed but will still contain micro-structure defects.

On the other hand, Group II (80 % silica nanosphere, 20 % metakaolin) has a greater density in comparison; there are less visible cracks, and the overall porosity is reduced. With the addition of silica nanosphere, packing of the active particles is most likely improved which can lead to an enhancement in the geopolymerization reaction, resulting in a denser structure. This denser morphology aids in the measured increase for the diametral tensile strength because of the improvements seen in

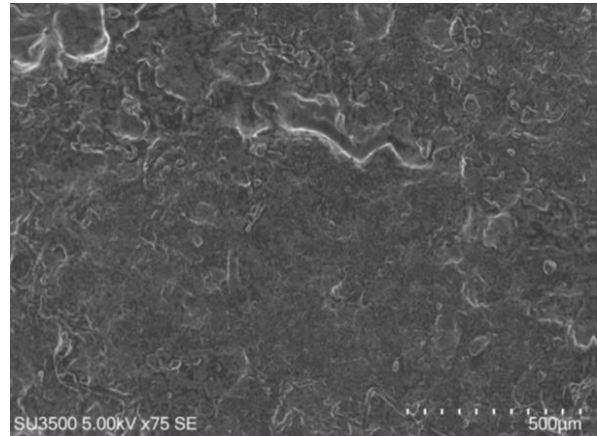


Fig. 8. A SEM image of Group III (Magnification 75×).

microstructure leading to a reduced stress concentration and overall improved mechanical performance. Group III (60 % zirconia, 20 % silica nanosphere, 20 % metakaolin) displays the most dense and homogeneous structure of the

three groups tested. The SEM image shows little porosity and limited cracks, indicating better densification. The inclusion of zirconia has demonstrated the high thermal stability and mechanical stability [33], which may help further enhance the geopolymer matrix wetter by reducing shrinkage and crack formations. The silica nanosphere also contributes to the refinement of the microstructure by filling in gaps within the geopolymer matrix and allowing for a more uniform geopolymerization throughout the specimen. This added structural integrity is reflected in the statistically highest diametral tensile strength for this test group indicating that the additional zirconia paired with the silica nanosphere has demonstrated an improvement in the mechanical properties of the metakaolin-based geopolymer significantly.

Beyond the visual densification is not the only factor to consider, the interaction mechanisms between nanoparticles and the geopolymer matrix might explain the observed improvements. Silica nanospheres act as nucleation centers for the N–A–S–H gel formation, which speeding up the early stages of geopolymerization, and providing a more uniform aluminosilicate network. On the other hand, zirconia can engage in chemical interactions with silicate species through the creation of Si–O–Zr bonds [34, 35], thus, reinforcing the interfacial region between filler and the matrix. These bonds are beneficial by providing improved load transfer and decreased microcracking at the interface [36]. Due to its high stiffness, Zirconia acts like a micro-scale crack deflector thereby inhibits the crack propagation paths and increasing resistance to tensile forces [37].

Conclusions

The study examined how incorporating zirconia and

silica nanoparticles influenced metakaolin-based geopolymer composites. For XRD, metakaolin was confirmed to have an amorphous silica along with monoclinic zirconia, tetragonal zirconia, and quartz, mullite, and hematite as crystal phases. SEM images depicted extensive morphology variations, as both silica nanoparticles and zirconia formed tighter microstructures than metakaolin alone, which resulted in higher density and lower porosity for the composites. The diametral tensile strength (DTS) of the geopolymer composite with only silica nanoparticles (80% by weight) was 2.24 MPa whereas the addition of 60% zirconia and 20% silica nanoparticles yielded a DTS of 3.61 MPa. The results indicate that silica nanoparticles and zirconia acted to strengthen the geopolymer matrix, where zirconia provided mechanical support and silica reinforced densification. The present findings align with previous studies that report silica and zirconia sized to the nanoscale have enhanced the mechanical performance of geopolymer composites. For future developments, the long-term durability, and thermal capabilities of the modified geopolymers will add valuable insight to its structural and functional uses. Due to their improved tensile response, densified microstructure, and incorporation of biocompatible ceramic phases, these nanoparticles-modified geopolymers could be considered for non-load-bearing biomedical applications, such as dental fillers, endodontic repair materials, or bone substitute scaffolds. Also, their improved stability indicates potential use in bioactive coatings or restorative materials requiring controlled mechanical performance.

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Підвищення властивостей геополімерів на основі метакаоліну: вплив додавання наночастинок цирконію та діоксиду кремнію

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Геополімери відомі своєю високою міцністю на стиск, але низькою міцністю на розтяг через крихку природу, що обмежує їх використання як конструкційних матеріалів. Тому важливим є підвищення їхніх механічних характеристик шляхом введення армувальних компонентів. У цій роботі досліджено вплив наночастинок діоксиду кремнію та цирконію на підвищення міцності на розтяг геополімерних композитів на основі метакаоліну. Геополімери отримували з використанням активатора на основі 8M NaOH та силікату натрію, який готували протягом 24 годин перед змішуванням у співвідношенні 2:1. Наявність аморфного діоксиду кремнію, моноклінної та тетрагональної фаз цирконію, а також кристалічних фаз у метакаоліні, зокрема кварцу, муліту та гематиту, підтверджено методом рентгенівської дифракції (XRD). Дослідження за допомогою сканувальної електронної мікроскопії (SEM) показали, що додавання як наночастинок діоксиду кремнію, так і цирконію призводить до формування більш щільної мікрокомпозитної структури з меншою пористістю. Випробування на діаметральну міцність при розтягуванні (DTS) через 28 діб показали, що введення 80% наночастинок діоксиду кремнію підвищує міцність на розтяг на 15,2%, тоді як суміш 60% цирконію та 20% наночастинок діоксиду кремнію забезпечує зростання міцності на 61,2% порівняно з контрольним зразком (з 2,24 МПа до 3,61 МПа). Отримані результати свідчать, що наноматеріали, такі як діоксид кремнію, сприяють ущільненню матриці, тоді як цирконій забезпечує структурне армування та покращення механічних властивостей. Результати узгоджуються з попередніми дослідженнями, які демонстрували синергійний ефект наночастинок діоксиду кремнію та цирконію для покращення характеристик геополімерів. Отримані дані також показують, що модифіковані геополімери можуть бути використані в застосуваннях, що потребують високої механічної міцності, однак для їх практичного використання у конструкційних та функціональних матеріалах необхідні додаткові дослідження довговічності та термічних властивостей.

Ключові слова: геополімер; цирконій; наночастинок діоксиду кремнію; золь-гель; діаметральна міцність на розтяг; морфологія.