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Sustainability evaluation, engineering properties and challenges relevant to geopolymer concrete modified with different nanomaterials: A systematic review

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ABSTRACT

Geopolymer, a novel binder material, possesses the potential to replace conventional cement completely. Recent studies have investigated the incorporation of various nanomaterials (NMs) into geopolymer concrete (GPC) to enhance its properties. Nanotechnology, an emerging field of study, has garnered significant attention in recent decades due to its groundbreaking research and practical applications. This comprehensive review aims to elucidate the effects of nanomaterial inclusion on the workability, strength, durability, and physical and microstructural characteristics of GPC. The properties have been meticulously examined, reviewed, and discussed. Over 190 research and review articles were reviewed, analyzed, and presented to develop a database containing critical properties of GPC modified with different doses and types of NMs. The influence of introducing diverse kinds and doses of NMs on GPC behavior was assessed. Historical trends, current tendencies, challenges, and the benefits and limitations of NM-modified GPC were explored. According to this review, incorporating NMs is promising for developing high-strength or high-performance GPC. It significantly improves mechanical, microstructural, and durability properties by providing additional calcium-silicate-hydrate, calcium-aluminate-silicate-hydrate gel, and nano-filling effects in the GPC matrix. This advancement will enable the construction industry to realize the potential of NM-enhanced GPC successfully. The present review demonstrated that the geopolymer concrete showed enhancements in engineering properties and effectiveness when modified with different types of nanomaterials and tested under different conditions. The current study also presented some challenges and research gaps that should be addressed in future research studies.

1. Introduction

The development of cement-based materials modified with nanomaterials has emerged as a promising avenue for enhancing the performance of construction materials to meet the increasing demands of modern infrastructure. With the advent of nanotechnology and its potential to revolutionize material science, researchers have extensively studied the application of nanomaterials in cement-based materials, such as geopolymer concrete, to improve their mechanical, durability, and functional properties [1]. These advancements in cement-based materials have garnered significant attention, given their potential to address the environmental and sustainability concerns associated with conventional concrete production [2–6]. It is well-established that cement manufacturing is one of the most significant sources of emitting carbon dioxide and other harmful gases globally. It releases approximately 4–7% of carbon dioxide into the environment [7]. Amongst materi-

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als utilized in construction, Portland cement holds 35% of gas outflow related to construction [8]. Manufacturing ordinary Portland cement (OPC) contains 65 to 75% of releases of total greenhouse gases (GHG) when producing concrete. Hence, every major country has now made it essential to regulate and reduce the outflow of carbon dioxide [9]. Moreover, to produce one ton of OPC requires approximately 2.75 tons of raw materials [10]; this is a very resource-intensive procedure as this method demands a massive number of natural materials, for instance, shale, lime, silica, and calcium, to make the clinker[11]. Every year one trillion liters of water for mixing is needed in the concrete and construction sector [12]. After manufacturing steel and aluminum, OPC is the third highest energy-intensive construction material; approximately 115 to 125 kilo-Watt-hour is required to produce 1 ton of OPC [13]. Though, OPC is still needed to make concrete because it is the primary binder material globally in the construction sector [14]. Hence, highly efficient, renewable, and non-renewable raw material is required for environmental protection and is not so intensive on energy and other resources. Developing sustainable materials to substitute OPC has become necessary as the world faces grave environmental issues. Geopolymer concrete technology was used as an appropriate, proper substitution for traditional concrete, which was first introduced in France in the 70 s.

Geopolymer is a polymer family consisting of alumino-silicates which is chemically synthesized by activating alkaline materials of different alumino-silicates materials or aluminum, silicon-rich agricultural and industrial waste products, for instance, silica fume (SF), wheat straw ash (WSA), granulated blast furnace slag (GBFS) [15], fly ash (FA) [16], palm oil fuel ash (POFA) [17], metakaolin (MK) [18] and bagasse ash [19]. The action mechanism of nanomaterials in geopolymer concrete primarily revolves around their unique characteristics at the nanoscale, such as high surface area, aspect ratio, and reactivity [20]. These nanomaterials, including nano-silica, nano-alumina, carbon nanotubes, graphene nanoplatelets, and nano-clay, can significantly influence the geopolymerization process, which is the fundamental reaction responsible for the formation of geopolymer concrete [21]. By promoting geopolymerization and providing additional reactive sites, nanomaterials can facilitate the formation of a denser and more compact microstructure, improving mechanical properties and durability. Furthermore, incorporating nanomaterials into geopolymer concrete can result in a finer pore structure, reduced permeability, and enhanced resistance to chemical attacks. The synergistic effects of nanomaterials can also impart advanced functionalities to the material, such as self-cleaning, air-purifying, and UV-blocking properties [22]. The comprehensive understanding of the action mechanisms of nanomaterials on geopolymer concrete has the potential to drive the development of innovative cement-based materials, thereby paving the way for more sustainable and resilient construction practices [23,24]. It was observed that the activation of alkaline in metakaolin utilizing a polymerization framework suggested explaining the development of zeolite precursors by an alkaline alumino-silicate solution [25]. Polymerization is the chemical reaction amid the binder source and the alkaline solution. The end product is a 3D ring-like structure and polymer chain Silica-Oxygen-Alumina-Oxygen bonds, as presented in Fig. 1.

1.1. The mechanism of Polymerization

Geopolymerization is an intricate, eco-friendly chemical process that forms inorganic polymers through the reaction of aluminosilicate materials and a highly alkaline activating solution. Aluminosilicate materials commonly used in this process include industrial byproducts such as metakaolin, fly ash, and ground granulated blast furnace slag (GGBFS), which are rich in silica (SiO_2) and alumina (Al_2O_3) compounds [27–29]. The geopolymerization process commences with the dissolution of the aluminosilicate source material in the alkaline solution, which typically consists of a mixture of sodium or potassium hydroxide (NaOH or KOH) and a source of a soluble silicate, such as sodium or potassium silicate [30,31]. The interaction of these components generates an intermediate gel-like structure containing silicate and aluminate species, also known as oligomers or monomers. The dissolution rate is determined by the aluminosilicate source's nature and composition, the alkaline solution's concentration, and the temperature.

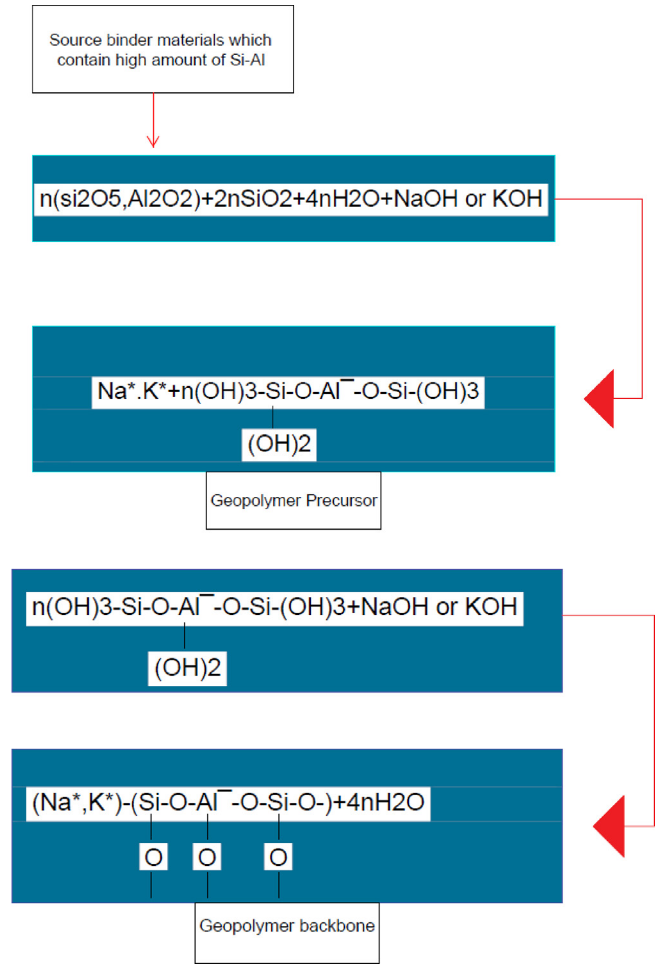

Fig. 1. Chemical reaction behind the process of geo-polymerization (Used from Open). Source [26]

Following the dissolution stage, the silicate and aluminate species undergo polycondensation, where they bond by sharing oxygen atoms, forming an amorphous, three-dimensional network structure. Within this network, the tetrahedral Si and Al atoms are connected by oxygen bridges, creating a framework with a negatively charged backbone. This negative charge is compensated by alkali metal or alkaline earth metal cations, such as sodium, potassium, or calcium, which occupy the cavities within the network and help stabilize the overall structure [32–34]. During the hardening phase, the geopolymer network experiences reorganization, densification, and strengthening through complex physicochemical reactions, including further polycondensation, rearrangement of bonds, and dehydration. The hardening rate can be influenced by factors such as the type and composition of the aluminosilicate source, the alkaline activator, the curing temperature, and the presence of additional additives or admixtures [35]. The resulting geopolymer material offers several advantages over traditional

Portland cement, including superior mechanical properties, resistance to aggressive environments, and lower thermal conductivity. Moreover, geopolymerization presents a sustainable alternative to conventional cement production, as it consumes less energy, requires fewer raw materials, and produces fewer greenhouse gas emissions [36]. This makes it a promising solution for mitigating the environmental impact of the construction industry and promoting the development of more sustainable, resilient infrastructure.

In the 1st phase, the dissolution of the source binder's elements of silicates and aluminum in a highly alkaline solution causes the development of aluminum and silicon oxide ions. In 2nd phase, a mix of alumino-silicate, silicate, and aluminate species is shaped, which causes the effect of an amorphous gel through the concurrent polycondensation gel method [37]. The chemical arrangement for the binder source and alkali chemicals influences the result of the polymerization method, and the polymerization is generally augmented at high temperatures. Due to this, geopolymer [GP] is the 3rd generation of binder material after the lime and OPC [38]. GP is an eco-efficient and sustainable material that releases around 75% less GHG than OPC concrete because of the high consumption of discarded materials in its mix proportion [39]. The mixing proportion of geopolymer concrete comprises a source of alumino-silicates binding material, alkaline activators, water, and coarse and fine aggregates. Because of the polymerization method, these materials lead to concrete almost similar to standard concrete [40]. 3D orienting of concrete, additive manufacturing, ceramics, geopolymer concrete, and other applications could take advantage of geopolymer technology. Different factors affect the characteristics and behavior of GPC, such as the chemical concentration of $Na(OH)_2$ [41], the ratio of Na_2SiO_3 to $Na(OH)_2$ [42], curing techniques, and curing period [43], the ratio of alkaline activators to binding material [44], the ratio of water to solids [45], type of source binding material and it's chemical composition [46], the proportion of silica to alumina in GP matrix [47], time of mixing and resting phase [48], the influence of admixture and extra water [49], and the proportion of coarse and fine aggregates [50]. Nanotechnology can monitor and restructure the matter at the atom and molecule stage in the scope of 1 to 100 nm and also contribute different properties and attributes at a size equal to an individual atom or molecule [51]. Nanotechnology is a growing research domain, with new knowledge and practical theories that have slowly attained distinction in the last twenty years.

Lately, work has been done to add nano-materials in different construction materials to improve their characteristics and develop concrete with enhanced properties [52]. Fig. 2(a) depicts the classification of nano-materials or nano-particles based on their origin, such as nano-structure and dimension [53]. These nanoparticles can be generally classified based on whether carbon organic elements, for example, inorganic or polymer elements like oxides of metal [54–59]. Utilizing these nanomaterials and reutilizing the industrial waste pozzolanic materials, for instance, slag and silica fume, is likely to lower the outflow of carbon dioxide and energy usage, hence attaining the sustainability criteria (economy, social, and environment) of the construction sector, see Fig. 2(b). Scientists are attracted to creating composite building materials modified with nano-materials because nano-materials (NMs) have special chemical and physical characteristics because of their particle's ultra-fine size [60]. NMs counting nano-alumina [61], nano-iron oxide [62], nano-ferric oxide [63], nano-calcium carbonate [64], nano-silica [65], nano-metakaolin [66], nano-clay [67], carbon nano-tubes [68], and multi-walled carbon nano-tubes [69] were generally utilized to improve the performance of conventional OPC-based concrete. NMs were added in GPC to improve geopolymer concrete's physical characteristics, strength, and durability [70]. NMs have a high surface area, which brands them greatly reactive material and highly influences the reaction [71]. Hence, NMs change the GPCs at the atomic stage, which results in considerable enhancements in fresh and hardened properties with no heat of hydration [72]. In some research, NMs were utilized in geopolymer composites as a purposeful material for non-structural purposes such as self-cleaning and anti-bacterial.

1.2. Utilization of nanomaterials in geopolymer Concrete

Incorporating diverse nanomaterials in geopolymer concrete has attracted significant interest due to their potential to improve the material's properties, making it a sustainable and competitive alternative to conventional concrete. Strength properties, surface energy, electron conductivity, chemical reactivity, morphology, and absorption of the GPC significantly variating by substituting from macro material to nano-material [75]. A wide variety of stud-

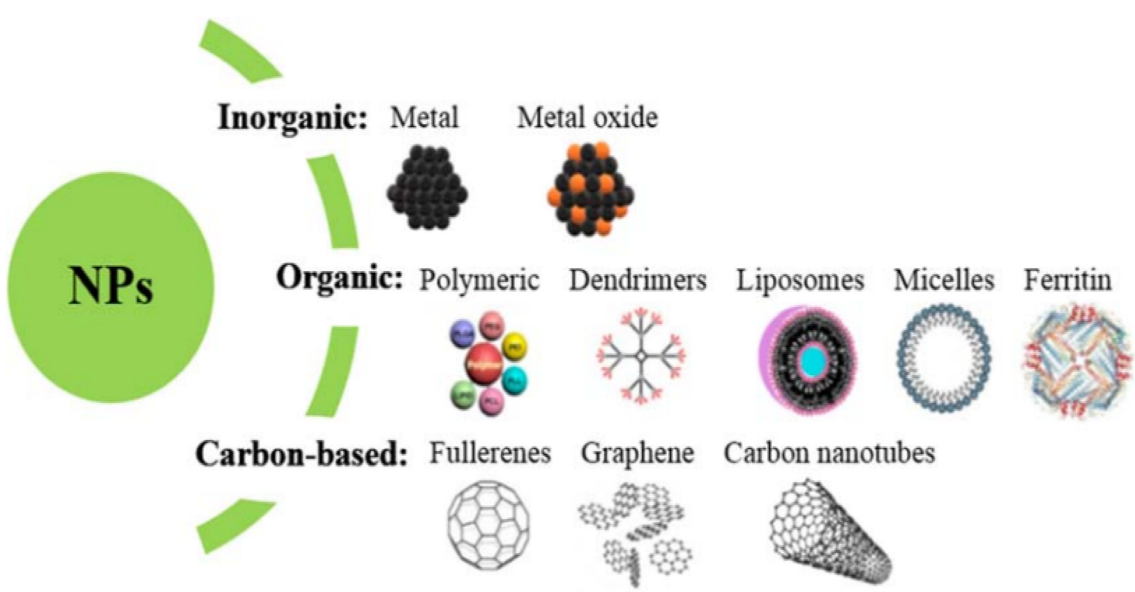

Fig. 2. a. Configuration of nano-particles on their nature of origin (Used from Open). Source [73]

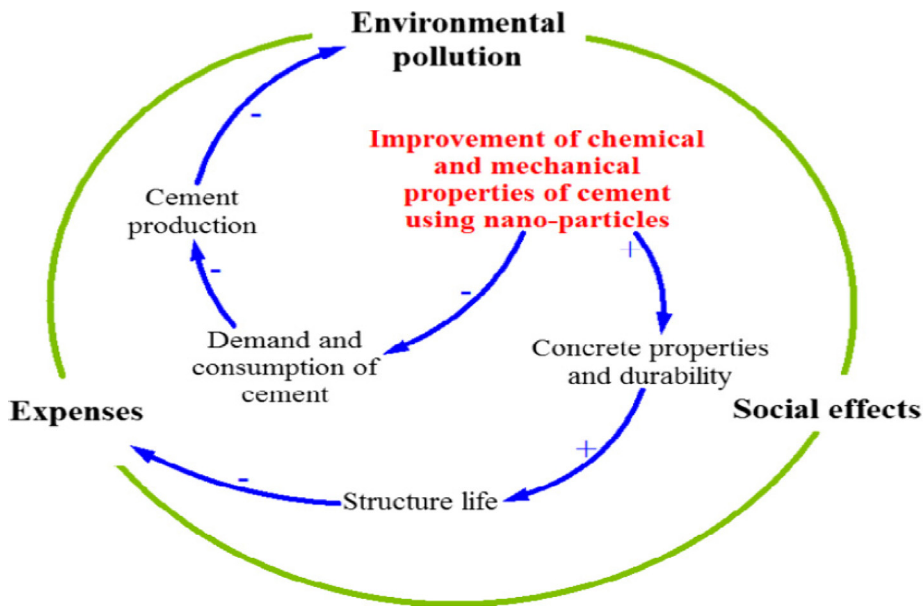

Fig. 2b. . Loop illustration signifying the role of nano-materials in the sustainable growth of the construction sector (Used as per Permission from Elsevier [74]).

ies has been performed in using NMs in the GPC to examine different properties of the concrete, such as durability and strength properties [76], fresh and micro-structural characteristics [77], resistance against fire [19], and permeability [78]. Because of the filling of voids and pores amongst particles of OPC by NMs, immobility happens in extra-water when the NMs are added to the OPC grains, called the filler effect.

Furthermore, the NMs contribute to the development of fresh C-S-H gel over the pozzolanic response, which improves the bond strength properties of the mixture by enhancing the ITZ amid the binder's paste and the aggregate [79]. GPC has insufficient compression strength and gradually grows when placed for curing in ambient surroundings [80]; though, it has brilliant compression strength in temperature curing, which limits the utilization of GPC as a pre-cast member in structure applications [81]. Hence, one way to consider this problem is to utilize NMs to quicken the chemical reaction in GPC to attain an optimized GPC with sufficient strength [82–86]. This can be obtained by modifying the GPC's microstructure at the atom level, which significantly enhances the fresh, strength, and durability properties of geopolymer concrete [87]. In past research, a vast scope of NMs such as nano-clay (NC) [88], carbon nano-tube (CNT) [2], nano-titanium (NT) [89], nano-metakaolin (NM) [90], nano-$CaCO_3$ (NCC) [91], nano-clay platelets (NCP) [70], graphene nano-platelets (GNP) [92], nano-silica (NS) [77], nano-alumina (NA) [93], multi-walled carbon nano-tube (MWCNT) [94], waste-glass nano-powder (WGNP) [95], nano-zinc oxide (NZn) [96] and nano-silica slurry (NSS) [97] was used to enhance different characteristics of geopolymer paste, mortar, and concrete. Based on data analysis and info in Fig. 3, nano-silica (NS) was the highly utilized NMs in geopolymer paste, mortar, and concrete. Also, this tendency towards NS was true for the OPC and traditional concrete because of the filling impact of pores and the pozzolanic behavior of nano-silica. SiO_2 is the main element of nano-silica, which can be found in amorphous or crystal shapes. Usually, nano-silica's amorphous shape was utilized to develop various kinds of concrete [98]. Nano-silica has formed from spherical shaped elements with a diameter of 140 to 150 nano-meters and a very high surface area of 200 to 220 m^2/gm developed by vaporizing SiO_2 amid 1600 to 1950 °C in the electric controlled furnace by lowering the quartz [99]. The particle size of nano-silica is mainly in the range of 10 to 640 nano-meters for different types of nano-silica products [100].

Nano-clay, characterized by its phyllosilicate structure, high aspect ratio, and large surface area, acts as a nano-filler, reducing porosity, and increasing density, ultimately improving the mechanical and rheological properties of geopolymer concrete. Carbon nanotubes, including CNTs and MWCNTs, exhibit remarkable mechanical, electrical, and thermal properties, enhancing tensile strength, fracture toughness, and crack resistance when uniformly dispersed within the geopolymer matrix. Due to its high photocatalytic activity, Nano-titanium imparts self-cleaning and air-purifying properties to the geopolymer concrete, allowing for the degradation of organic pollutants and contributing to a healthier urban environment. Nano-metakaolin, a highly reactive pozzolanic material derived from thermally activated kaolinite clay, enhances mechanical properties and durability by providing additional reactive sites for geopolymerization, promoting densification, and increasing resistance to chemical attacks. Nano-$CaCO_3$ particles contributed to the densification of the geopolymer matrix, leading to improved compressive strength and reduced permeability while also accelerating the geopolymerization process. Nano-clay platelets and graphene nano-platelets can enhance the concrete's mechanical and barrier properties by forming a tortuous path for the diffusion of aggressive agents, preventing ingress and reinforcing the material. Nano-silica and nano-alumina promote geopolymerization and densification of the microstructure, improving the mechanical properties and durability of the concrete by providing additional reactive sites and facilitating the formation of a denser geopolymer gel. Waste-glass nano-powder, a supplementary cementitious material, forms additional geopolymer gel, while nano-zinc oxide improves the concrete's photocatalytic, self-cleaning, and UV-blocking properties. Lastly, nano-silica slurry enhances geopolymer concrete's mechanical properties and durability due to its high pozzolanic activity and ability to fill voids in the matrix. The significant improvements from the inclusion of the above-stated types of NMs include (a) enhanced hydration and polymerization of binder source materials, (b) high strength characteristics, (c) making the microstructure denser, (d) lower the permeability of composites, and (f) enhanced resistance in aggressive surroundings.

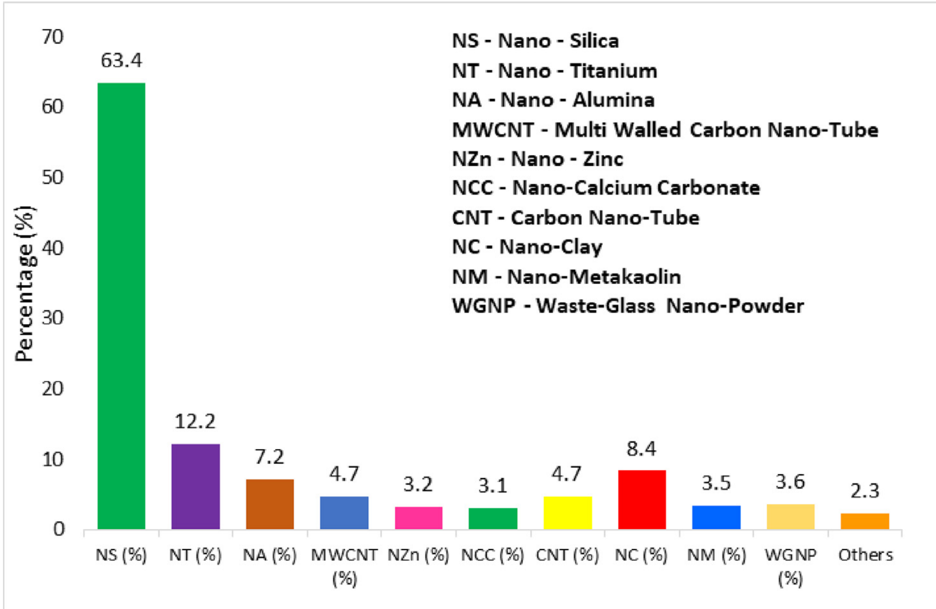

Fig. 3. Frequency of utilization of nanomaterials in the production of GPC (Data from references [87,92,96,101–106]).

1.3. Significance of present work

Significant research studies have been performed over the last few years on adding different NMs in GPC. Past review papers have just summarized the impact of NMs in GPC but didn't offer comprehensive data. Also, various newly published research papers were not added to those previous review articles. To do this, all the past and updated research work in this domain were studied to highlight the influence of different kinds of NMs on the strength, durability, and microstructural characteristics of geopolymer concrete (GPC) and to analyze and review the results systemically. According to the authors' best information, no updated review has been presented that comprehensively reviews and explains the role of nanomaterials on the strength, durability, and microstructural characteristics in the progress of GPC, which marks the originality of the current review paper. The test properties reviewed are compression strength, modulus of elasticity, split tensile strength and flexural strength, sorptivity, residual compression strength, acid attack test, resistance against chloride penetration, and concrete loss in weight due to sulfate attack. Furthermore, a review of microstructural analysis was done comprehensively covering x-ray diffraction (XRD), scan electron microscopic test (SEM), and Fourier transom infrared spectroscopy (FT-IR) to establish the part of NMs in improving the microstructural properties of GPC modified with nanomaterials. Lastly, requirements for future research, limitations, and challenges are also presented, which should be tackled to fill that research gap. This review will expand the prospects of scholars and the construction sector by offering essential data about the impact of introducing various kinds of NMs on the characteristics of GPC.

2. The procedure for collecting data for the current Review

Extended research was performed on the different academic platforms on the internet to collect data. The authors obtained a vast variety of articles related to the impact of various types of NMs (NT, NC, NA, NCC, MWCNT, NCP, GNP, NS, NM, CNT, CNS, WGNP, NZn, and NSS) on the characteristics of different composites of geopolymer, for example, high-strength GPC, conventional GPC, fiber-reinforced GPC, self-compacting GPC, recycled aggregate GPC, light-weight GPC, geopolymer paste, and geopolymer mortar. The time range of the published articles dealing with the utilization of NMs in GPC was published online from 2014 to 2022. Extended information counting all the data needed from the past papers, for example, type of nanomaterials, characteristics of nanomaterials, type of GPC, and kind of binder source, are presented in Table 1; complete information of the examined aspects was obtained. The data and information collected from past online articles were utilized to investigate how often each nanomaterial is employed in GPC. Furthermore, detailed graphs using past information were made and conferred in detail. The most essential and general characteristics of GPC that were accessible in the past papers as presented in Table 2; for example, modulus of elasticity, compression strength, split tensile strength and flexural strength, sorptivity, acid attack test, resistance against chloride penetration, concrete loss in weight due to detrimental elements, x-ray diffraction (XRD), scan electron microscopic test (SEM) and Fourier transom infrared spectroscopy (FT-IR) were depicted and conversed comprehensively. As the various kinds of NMs have a comparatively identical effect on the performance of GPC, they are not classified into multiple segments. Finally, future demands of research on this topic and challenges related to this topic are also offered. More details about the method of this review paper are provided in the shape of a flow-chart as presented in Fig. 4.

3. Strength characteristics of geopolymer concrete with nanomaterials

This portion depicts and analyzes the highly vital and broadly examined strength characteristics revealed in the past articles. The strength characteristics conferred in this review add splitting tensile strength, flexural strength, modulus of elasticity, and compression strength.

3.1. Compression Strength

Compression strength is a vital strength attribute for assessing the behavior of concrete as it signifies the overall quality of concrete [123]. Different test procedures are utilized to evaluate concrete samples' compression strength, such as ASTM C39 [124] and

Table 1
Characteristics, types, and doses of nanomaterials observed in the past papers to improve GPC.

Source Binder	Type of NMs	The proportion of NMs (%)	Characteristics of NMs	Ref.
Fly-ash	Nano-silica	0 and 6	Density (g/cm^3) = 2.3, pH = 9 – 9.5, Particle size = 4 – 15 nm	[107]
Fly-ash	Nano-silica	0 and 3	99.7% Silicon dioxide	[108]
Fly-ash	Nano-silica	0.5, 1 and 1.5	pH = 8 – 9, dispersion = 3.3 – 4.8, surface area = 199 m^2/g, Purity = 99.8%	[109]
Fly-ash and Slag	Nano-silica and micro-silica	1, 1.5 and 2	N/A	[77]
Slag	Nano-silica and micro-silica	0.5, 1 and 3	Blain (m^2/g) = 192, Density (kg/m^3) = 199, Purity (%) = 99.7	[78]
Fly-ash and Rice husk ash	Nano-Silica	2, 4 and 6	Surface area = 199 m^2/g, Purity (%) = 99.7 and Particle size = 8 – 11 nm	[19]
Slag	Nano-clay, nano-silica, nano-alumina	1.5, 3 and 5	Density (g/cm^3) = 0.7, Blain (m^2/g) = 250, Particle size = 1 – 2.5 nm	[93]
Fly-ash and Slag	Nano-clay	4, 6, 8 and 10	N/A	[88]
Fly-ash and Slag	Carbon nanotube, Nano-clay	0.01 and 0.02	Inner diameter = 2 – 14 nm, length (mm) = 15 – 95 mm, Outer diameter = 50 nm	[2]
Slag	Nano-silica	2, 4, 6 and 8	Surface area = 200 m^2/g, SiO2 = 99.6 (%), Particle size (nm) = 13	[90]
Fly-ash	Nano-TiO_2	1, 2, 3, 4 and 5	Particle size (microns) = 10 – 20, 59% titanium and 415 oxygen	[110]
Natural pozzolana	Nano-silica	1, 2.5, 5 and 7	Density = 1.4 g/cm^3, Size of Particle = 34 nm, Surface area (m^2/g) = 75	[111]
Natural pozzolana	Nano-silica	1, 2.5, 5 and 7	pH = 9, particle size = 32 nm, surface area = 78 m^2/g, content of solid = 48%	[112]
Natural pozzolana	Nano-silica	1, 2.5, 5 and 7	Viscosity (cps) = 14, pH = 9.5, nm, surface area = 78 m^2/g,, particle size = 33	[113]
Metakaolin	Nano-silica	1, 2 and 3	N/A	[65]
Fly-ash	Nano-silica, CNT, Nano-TiO_2	0 and 1	N/A	[114]
Metakaolin	Nano-silica	1 and 2	Specific gravity = 2.32, Transparency (%) = 98.9, Surface area (m^2/g) = 202	[115]
Fly-ash	Nano-silica nanoparticles	2, 4, 6 and 8	Size of Particle = 9 nm	[116]
Slag	Nano-silica	1, 2 and 3	N/A	[117]
Slag	Nano-silica	0 and 2	Surface area (m^2/g) = 44, Particle size = 28 nm, purity = 99.2 (%)	[118]
Slag and Silica fume	Nano-Silica	2.5, 5 and 10	Carbon nanotube had a diameter of 15 to 115 nm, a few micrometers in length.	[119]

Table 2
Various test properties of GPC in previous articles.

CTS	FS	STS	RCPT	MOE	W	P	D	WA	SEM	SP	Ref.
✓	–	–	–	✓	–	✓	✓	✓	✓	✓	[114]
–	–	–	–	✓	✓	–	–	✓	✓	✓	[113]
✓	✓	–	✓	✓	–	✓	✓	✓	✓	–	[111]
✓	✓	✓	✓	✓	✓	–	–	✓	–	✓	[110]
✓	–	✓	✓	✓	✓	✓	–	✓	✓	✓	[97]
✓	✓	✓	–	✓	✓	✓	✓	✓	–	✓	[91]
✓	–	✓	✓	✓	✓	✓	✓	✓	✓	✓	[97]
✓	–	✓	–	✓	✓	✓	✓	✓	✓	✓	[95]
✓	–	✓	✓	✓	✓	✓	✓	✓	✓	–	[94]
✓	✓	✓	✓	✓	✓	✓	✓	–	✓	–	[88]
✓	✓	✓	–	✓	✓	–	✓	✓	✓	✓	[87]
✓	✓	✓	✓	✓	✓	✓	✓	–	✓	–	[19]
✓	–	✓	✓	✓	✓	✓	–	✓	✓	–	[77]
✓	✓	✓	✓	✓	✓	–	–	✓	✓	✓	[108]
✓	–	✓	✓	–	✓	✓	✓	–	✓	✓	[107]
–	✓	–	✓	✓	✓	–	✓	✓	✓	–	[70]
✓	✓	✓	✓	–	✓	✓	✓	✓	✓	✓	[120]
✓	–	✓	✓	✓	✓	✓	✓	✓	✓	✓	[115]
✓	–	–	✓	✓	✓	–	✓	✓	✓	✓	[121]
✓	–	–	–	✓	✓	–	✓	✓	✓	✓	[122]

Note: CTS – Compressive strength, **FS** – Flexural strength, **STS** – Splitting tensile strength, **RCPT** – Rapid Chloride Penetration Test, **MOE** – Modulus of elasticity, **W** – workability, **P** – Porosity, **D** – Density, **WA** – Water Absorption, **SEM** – Scan Electron Microscope test, **S**P – Sorptivity test.

BS EN 12390 [125]. The compression strength was thoroughly examined in the past research for GPC that introduced distinct types of Nanomaterials. The effect of the addition of NMs on the compression strength of GPC is depicted in Figs. 5 and 6 at 7 and 28 days of the curing stage. Figs. 5 and 6 present that incorporating NMS improves the GPC's compression strength to only the optimal doses of NMs. Studies have been performed on the workability, strength, and microstructure characteristics of fly ash/slag-based GPC with nano-silica at various proportions. The authors reported that all the mixes of nano-silica's compression strength were improved than the reference mix with no nano-silica. The highest compression strength was observed at a 2% dose of nano-silica, which enhanced the compression strength by 12% compared with the reference mixture at the curing phase of 4 weeks at room condition. Strength enhancement is ascribed to the filling ability of nanomaterials in the GPC by silica particles, making the inside concrete more packed and denser. Furthermore, the chemical arrangement of nano-silica with abundant SiO_2 quickens the geopolymer reaction and forms the geopolymer binder sturdier, ultimately improving the sample's strength. Moreover, the authors preferred 2% of nano-silica could be the optimized amount for the enhancement of compression strength, as after 2% of nano-silica, the strength was observed to be reduced because of the abundant amount of un-reacted particles of nano-silica in the mix, and this ample proportion of nano-silica led to flocculation amid the particles of nano-silica which might have barred the dis-solution of SiO_2

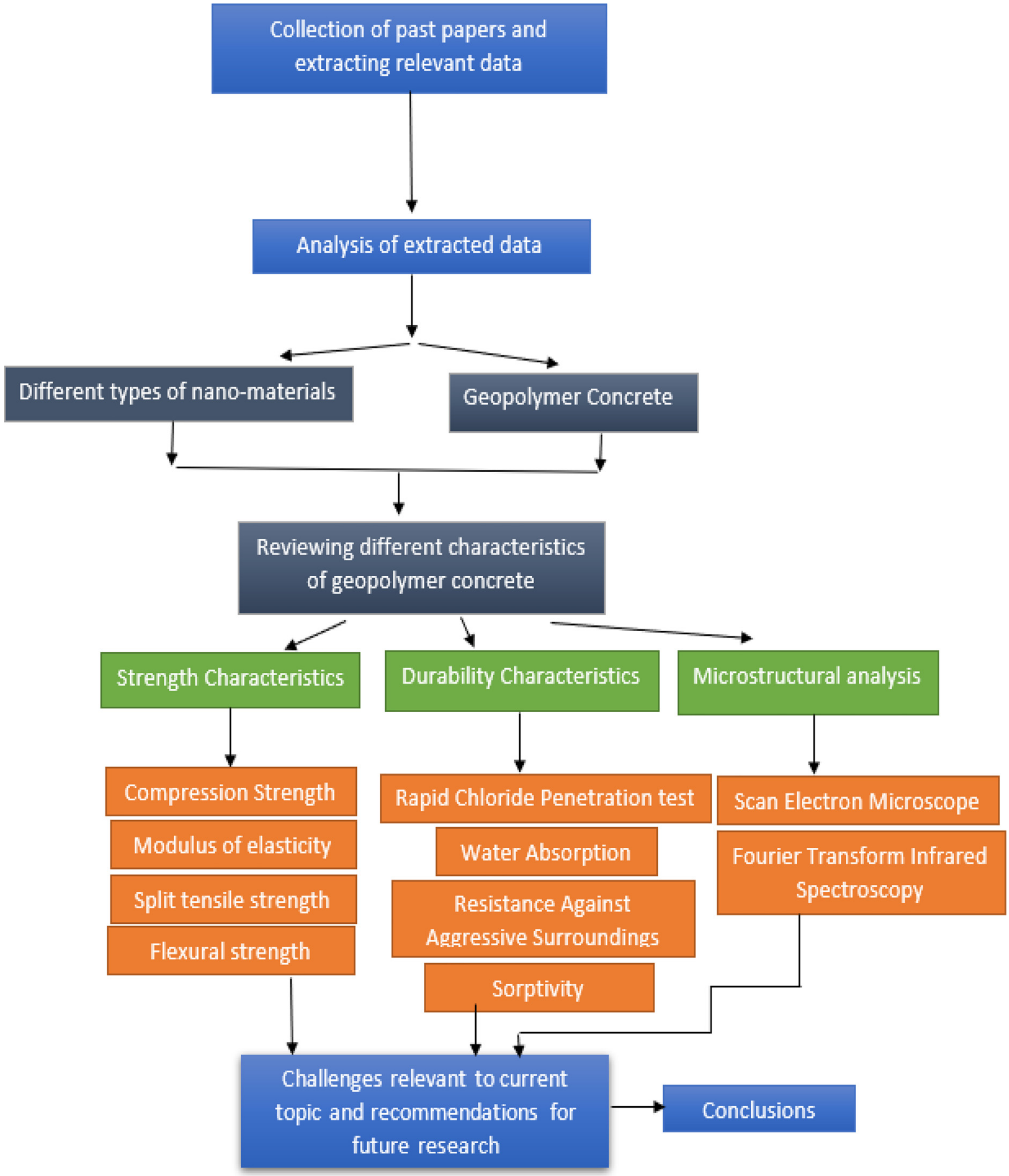

Fig. 4. Flow chart illustrating the design of the current review paper.

hence leads to the formation of voids; as a result, it leads to the formation of voids, this reduces the compression strength of GPC [77].

The same results have also been observed in past studies [117,126], which observed that including nano-silica enhances the compression strength of GPC. Nuaklong et al. [127] reported that 2% nano-silica in geopolymer concrete could improve compression and splitting tensile strength. Beyond 2% of nano-silica, it reduces strength properties. Also, Lincy et al. [115] reported that 0.5% inclusion of nano-silica improved the GPC's compression strength, and then a decrease in the compression strength was observed. Though Ramezanianpour et al. [119] and Ibrahim et al. [113] reported that the GPC compression strength enhanced as the dose of NMs raised to 4%, and beyond 4%, the strength reduced. The compression strength improved by 2.3%, 14.2%, and 2.1% at 2%, 4%, and 6% of carbon nano-tubes at the curing age of 28 days [119], while this improvement in compression strength was 0%, 7.9%, 22.9% and 19.7% at 1.5, 3, 4.5 and 6% of nano-silica at curing phase of 28 days [156].

Similarly, Khater et al. [128] examined the physical and strength characteristics of nano-silica influence on the GPC. Different percentages of nano-silica varying from 0 to 7% were added. The result of the study report revealed that adding nano-silica enhances the compression strength of the GPC up to 25%, and further addition of nano-silica will ultimately lower the compressive

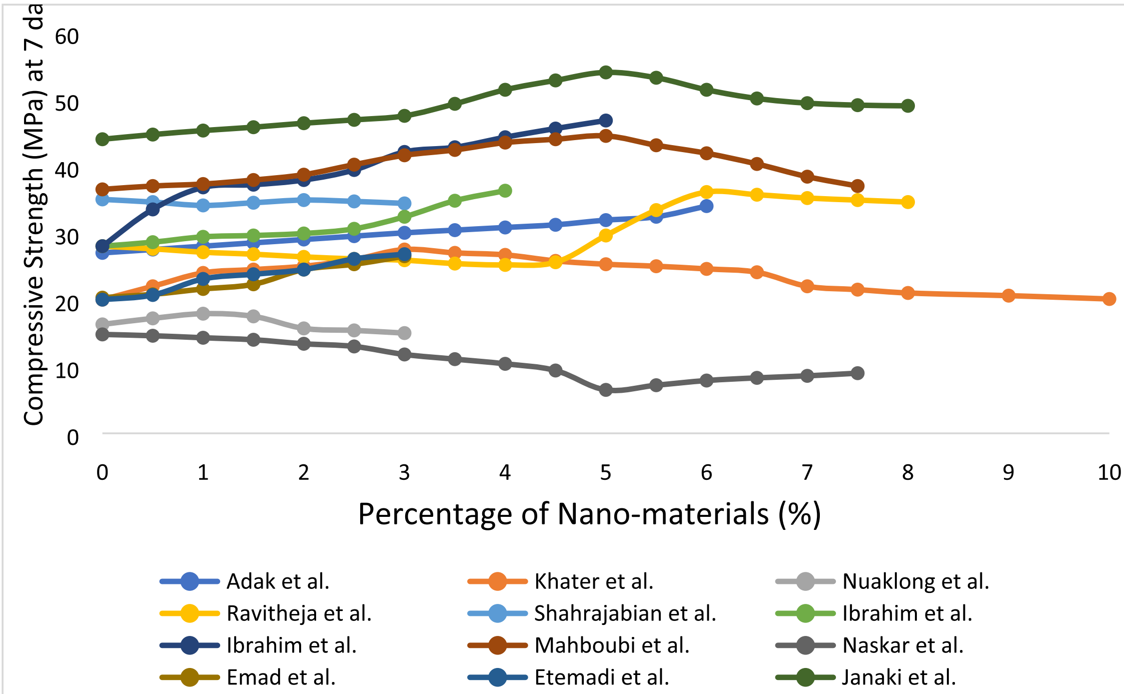

Fig. 5. Compressive strength of GPC at different percentages of NMs at the curing of 7 days.

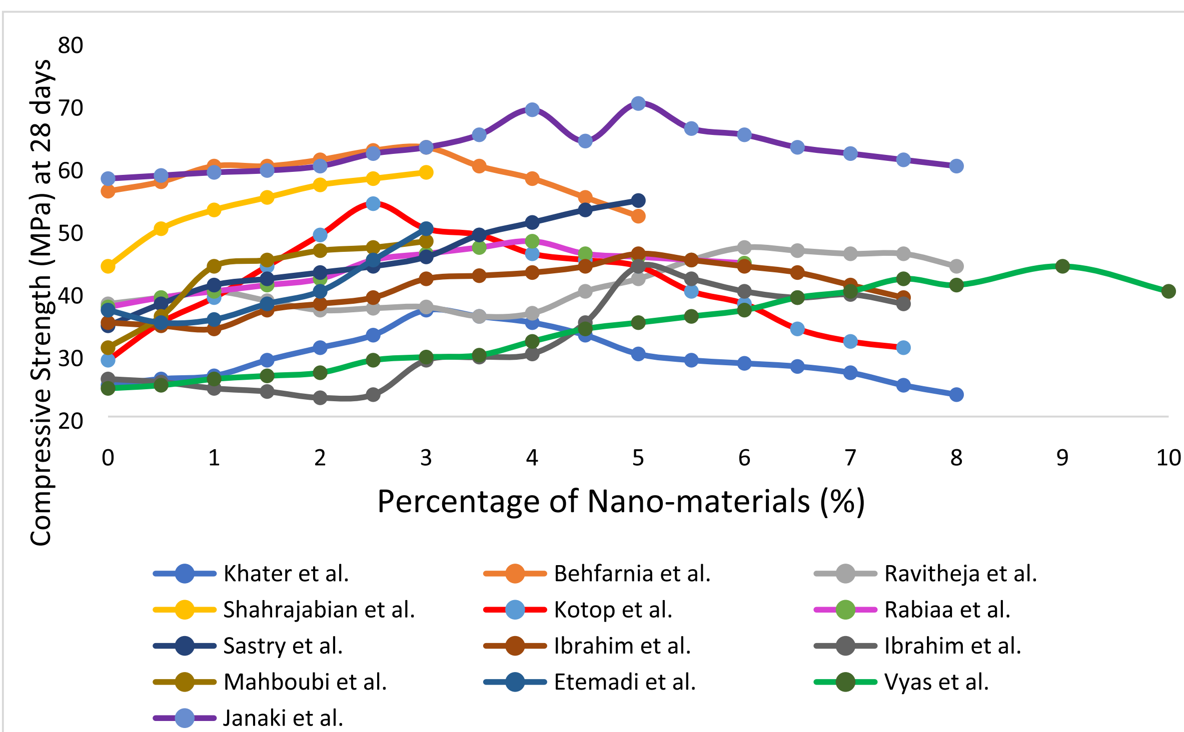

Fig. 6. Compressive strength of GPC at different percentages of NMs at the curing of 28 days.

strength because of the flocculation of the particles of nano-silica. The highest compression strength was 35 MPa for a 4% nano-silica compared to 25 MPa of the reference sample with no nano-silica. Also, the optimized nano-silica dose was 4%, as revealed in other studies [129,130]. Behfarnia et al. [78] demonstrated that replacing 4% nano-silica improves the compressive strength at 28 days by 11%, and using nano-silica beyond this range will cause a reduction in strength. This could be ascribed that nano-silica contributed to the pozzolanic reaction to form an additional calcium-silicate-hydrate gel and fills the pores in the concrete mix at the nano-scale. In contrast, the decrease in compression strength was ascribed to the flocculation of nano-silica particles in the GPC mix, trailed by the development of voids in the GPC's mix [78].

Regarding the utilization of nano-clay and nano-metakaolin in GPC, research was performed to assess the influence of including nano-clay on the durability characteristics of GPC. The research results signified that the compression strength was enhanced by incrementing the amount of nano-clay. The compression strength of GPC was improved by 1.3 and 1.5 times the control sample at a 3% amount of nano-clay at the curing phase of 1 and 4 weeks [129]. Ravitheja et al. [88] revealed that adding nano-clay up to 5% enhances the compression strength of GPC; after this dose, the strength reduces. The authors observed that at 5% nano-clay, the highest strength achieved was 33, 38, and 49 MPa compared with the reference GPC, which had a compressive strength of 25, 31, and 38 MPa at the curing stage of 7, 21, and 28 days.

Furthermore, an empirical lab study was performed to examine the impact of nano-metakaolin on the characteristics of GPC. The authors utilized 0, 3, 6, 9, and 12% of nano-metakaolin to enhance the properties of GPC. Compressive strength was improved by 11% and 17%, then the reference sample at 9% nano-metakaolin at 7 and 28 days of curing. It was reported that 9% nano-metakaolin is optimized for GPC [90]. This improvement in compressive strength is ascribed to the reason that ITZ is refined with the needed amount of nano-metakaolin, which decreases the content of porosity and improves the firmness of the samples; therefore, compressive strength was enhanced. Though, the decrease of compression strength after 9% nano-metakaolin could be ascribed to the flocculation amid nano-particles of nano-metakaolin happened, which caused the formation of pores that might also be attributed to the unfinished hydration reaction [90]. Moreover, Shahrajabian et al. [93] noted that including nano-clay and nano-alumina reduced the compression strength of slag-based GPC at the curing phase of 7 and 28 days, while at 90 and 120 days, enhancement in the compression strength was observed. Based on the research studies that have been performed to examine the impact of various types of nano-materials on the different properties of GPC, an enhancement in the compression strength was observed at various doses of nano-silica [131], nano-clay [101], graphene nano-platelets [92], multi-walled carbon nano-tubes [132], carbon nano-tube [133], nano-zinc oxide [105] and nano-TiO_2 [134], were added to the GPC.

3.2. Modulus of elasticity (MOE)

MOE is an essential characteristic of construction material, which includes different types of concrete (lightweight, geopolymer, high strength, etc.); it offers information about the material's stiffness within the proportional limit. Geopolymer concrete with a high MOE offers good resistance against an external load. ASTM C469 [135] is utilized to evaluate the MOE of GPC. When studying pertinent research articles to assess the impact of NMs on the MOE of GPC, it was observed that the quantity of studies examining the effect of various nanomaterials on the GPC's MOE is lesser than the strength properties. The results of the past studies are depicted in Fig. 7.

Adak et al. [107] revealed that approximately 22% of the MOE was enhanced than the reference sample by introducing 7% of the NS to the GPC. Similarly, an empirical study was performed to improve the physical strength, durability properties, and microstructural behavior of natural pozzolana-based GPC modified with different doses of NS. The authors reported that the MOE was enhanced by up to 45% with raising nano-silica and reduced at 28 and 90 days of the curing stage. For example, the GPC's MOE was improved by 10.1%, 25.3%, 98.2%, and 86.5% at 2, 4, 6, and 8% doses of nano-silica [112]. Furthermore, the lab studies have shown the impact of various doses of waste-glass nano-powder (0%, 5%, 10%, 15%, and 20%) on the microstructural and strength properties of slag-based GP composite. The authors reported that, compared to the reference specimen, with a MOE of 13.9 GPa, the MOE was enhanced to 15.2 GPa at 5% of WGNP, but the MOE was reduced from 15.2 GPa to 14.2 GPa at 10% of WGNP. Moreover, the MOE of slag-based geopolymer composite reduced from 13.7 to 13.4 GPa when waste-glass nano-powder was increased from 15% to 20% [136]. The same test outcomes have been noticed by Huseien et al. [137]. The decreased MOE was ascribed to the low calcium amount of slag-based GP composites comprising less than 10% waste-glass nano-powder [137]. As per the observations of Rovnanik et al. [138], the MOE was enhanced as the dose of multi-walled-carbon-nano-tubes was increased in the fly ash-based geopolymer composites. The MOE was improved by 5.1%, 12.3%, 17.5%, and 15.8% at 0.06%, 0.12%, 0.18%, and 0.24% doses of multi-walled-carbon-nanotubes correspondingly, in comparison to the reference specimen of fly-ash-based geopolymer composites with no number of multi-walled-carbon-nanotubes. Zhang et al. [106] revealed that the MOE was enhanced by introducing 2% nano-silica to the fiber-strengthened geopolymer composite. This is because of silica's nano-pozzolanic activity, which causes extra gels of aluminosilicates in the geopolymer composite, accompanying the Silica-Oxygen bonds [139].

Furthermore, Ngernkham et al. [140] reported that with the inclusion of nano-silica and nano-alumina to the higher calcium fly-ash-based geopolymer composites cured at room temperatures, the MOE inclined to increase due to the inclusion of the nano-materials which results in the geopolymer composite being dense and firm as compared to a reference sample. The improvement in the MOE was 56.4%, 70.4%, and 36.3% at 1.5%, 3%, and 4.5% doses of nano-silica to the reference sample with no amount of nano-silica at the curing phase of 90 days. The same results were observed with the MOE of geopolymer composites modified by adding nano-alumina. A lab study examined the impact of graphene nano-platelets on the durability and strength characteristics of fly-ash-based geopolymer concrete. It was observed that as the graphene nano-platelets were raised, the MOE was also enhanced. The MOE was improved by 36.4%, 43.3%, and 85.2% at 0.3%, 0.6% 0.9% of graphene nano-platelets compared to the control sample with no graphene nano-platelets [92]. Luz et al. [133] observed that including carbon-nano-tubes in geopolymer composites leads to enhancing the modulus of elasticity.

3.3. Splitting tensile strength

This is one of the vital strength properties of concrete, which could be evaluated by following the standards set by the ASTM C496 [141] or EN 12390 [142]; on the other hand, there are also some other tests, such as the Brazilian test or indirect test which could also be used for determining the concrete's tensile strength. As concrete is usually susceptible to tensile load due to its inherent low strength in tension, it is essential to determine its tensile strength. Among different materials, nanomaterials could also be utilized to enhance the geopolymer concrete's tensile strength. Fig. 8 presents the test results of past research on the impact of different nanomaterials on the splitting tensile strength of GPC.

Experimental work was performed on the durability performance of GPC by adding various doses (0% – 3%) of nano-silica and nano-clay. The researchers observed that with the increase in the amount of nano-silica, the splitting tensile strength of the GPC was improved. At curing 28 days, the splitting tensile strength was enhanced by 17%, 29%, and 34% at 1%, 2%, and 3% doses of nano-silica compared with the reference sample. At 1%, 2%, and 3% doses of nano-clay, the splitting tensile strength of GPC was observed to be enhanced by 29%, 35%, and 34% compared with the reference sample with no dose of nano-clay [65]. Nuaklong et al. [127] studied the inclusion of nano-silica on the behavior of fly ash-based geopolymer recycled aggregate concrete. The authors noticed that the splitting tensile strength of GPC with no nano-silica was 2.65 MPa, and the uppermost splitting tensile strength was 3.1 MPa which was attained at 1% dose of nano-silica and

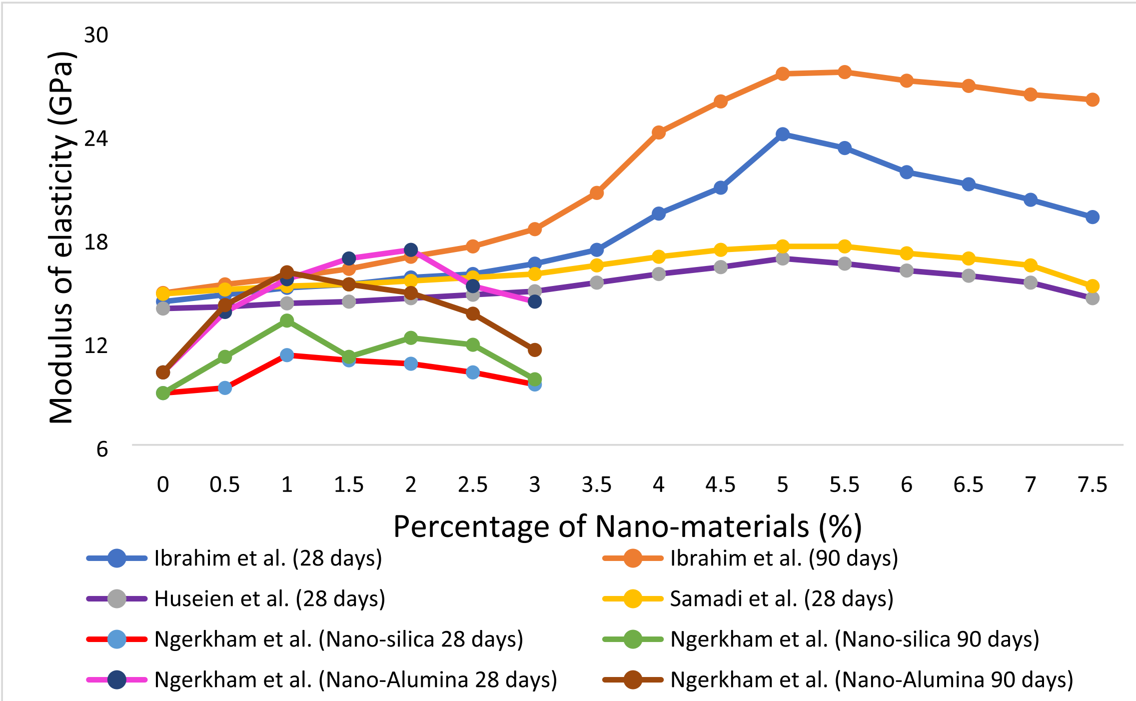

Fig. 7. Modulus of elasticity vs. Different types and amounts of NMs in GPC.

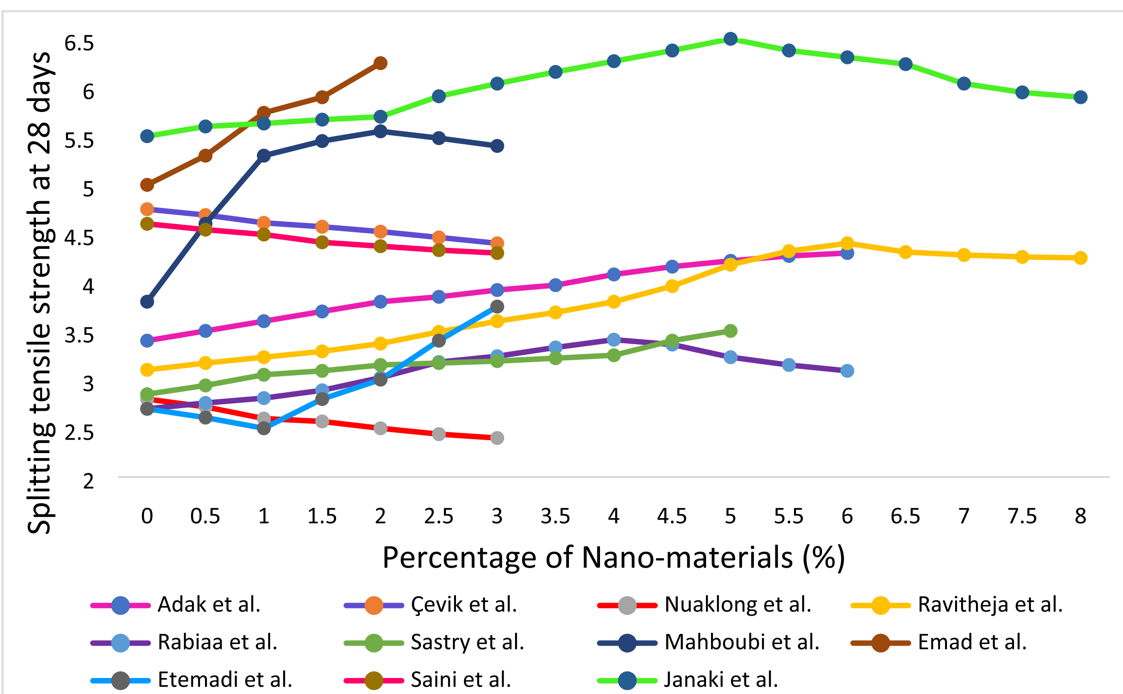

Fig. 8. Splitting tensile strength of GPC at different percentages of NMs at the curing of 28 days.

the splitting tensile strength was slightly decreased by introducing more amount of nano-silica. The reason behind the enhancement in splitting tensile strength at an optimal number of nanomaterials is the same as discussed in the compressive strength section. The same outcomes of enhancing the splitting tensile strength of GPC with the inclusion of nano-silica could be noted in other research, even though different proportions of nano-silica were utilized in those researches [117,118]. Lab work was performed to observe the impact of nano-silica and nano-metakaolin on the characteristics of GPC [90]. The authors utilized 0%, 2%, 4%, 6%, and 8% doses of nanomaterials. The authors noted that the splitting tensile strength was enhanced to only an optimal level with the addition of nanomaterials of NMs. The highest splitting tensile strength was revealed at a 4% proportion of nano-silica, about 20% more than the reference sample.

For nano-metakaolin, the authors demonstrated that 6% was the optimal dose at which the peak splitting tensile strength of 3.9 MPa, was noted, while in the reference sample, the split tensile strength was 2.6 MPa. Sastry et al. [110] studied the impact of nano-TiO_2 on the durability and strength properties of GPC. The authors utilized various doses of nano-TiO_2, revealing that by increasing the amount of nano-TiO_2, the splitting tensile strength was improved with it. At 28 days, the splitting tensile strength was enhanced by 8, 10, 11, 15, and 19% at the nano-TiO_2 dose of 1%, 2%, 3%, 4%, and 5% about the control sample with no nano-TiO_2. Carbon nanotubes were used to evaluate the strength and durability characteristics of slag and silica fume-based GPC. The authors noted that with the inclusion of carbon nano-tubes, the splitting tensile strength of GPC was enhanced by 3.9, 18.9 and 0.81% at 3%, 6%, and 9% doses of carbon nano-tubes, in comparison to reference samples with no carbon nano-tubes [143]. The research was performed to examine the impact of waste-glass nano-powders on the strength and durability attributes of slag-based GPC. The authors noted that with the introduction of waste-glass nano-powders, the splitting tensile strength of GPC was enhanced by 22% at 5% waste-glass nano-powders, and after that, the strength was reduced. The improvement in splitting tensile strength could be because of the addition of nano-materials, which densify the microstructure of GPC and improves the hydration characteristics [137].

3.4. Flexural strength

This test indirectly measures the concrete's tensile strength. Flexural strength is essential for concrete members which bend under the action of external loads, such as concrete beams, rigid pavements, slabs, etc. This test follows the standards set by ASTM C293 [144], BS EN-12390, and ASTM C78 [145]. Fig. 9 summarizes the test results of past research into the impact of different kinds of nanomaterials on the flexural strength of GPC. Because the inclusion of nanomaterials considerably enhances the concrete's matrix and decreases voids and cracks, the flexural strength of GPC could be improved by adding nano-materials at an optimal level.

Rabiaa et al. [90] performed experimental work to observe the impact of introducing nano-metakaolin and nano-silica on the various attributes of GPC. The authors observed that flexural strength was enhanced up to 6% dose of nano-metakaolin; afterward, the flexural strength was reduced. The flexural strength was 4.8, 5.2, 5.5, 5.9, and 5.7 MPa at 0%, 2%, 4%, 6%, and 8% nano-metakaolin; the highest flexural strength was noted at a 6% dose of nano-metakaolin. Similarly, the flexural strength of geopolymer concrete was improved by adding nano-silica up to 4% dose; above this dose, the flexural strength was reduced. The highest flexural strength was nearly 25% more than the GPC with no amount of nano-silica. Furthermore, Fouad et al. [118] studied the effect of various doses of nano-silica on slag-based GPC's strength characteristics. The test outcomes showed that the slag-based GPC's flexural strength was enhanced by 23% at the existence of a 2% dose of nano-silica at the curing stage of 28 days, compared to reference slag-based GPC with no proportion of nano-silica. Moreover, the authors also noted that the inclusion of nano-silica didn't impact the shape patterns of the cracks, and the failure of the plan of slag-based GPC samples almost broke at the specimen's mid-point. This can be ascribed to the homogeneity of the modified GPC samples. The same test results of enhancement of flexural strength of GPC could be noted in more research. However, different doses of nano-silica were utilized [146]. Saini et al. [146] revealed that, at curing days 28, 56, and 90, the inclusion of 2% nano-silica enhances the flexural strength of slag-based GPC by 6.8, 9.7 and 9.4% in comparison to reference specimens. Sastry et al. [110] examined the effect of different percentages of nano-TiO_2 on the mechanical and durability properties of GPC; the authors revealed that the flexural strength was improved as the dose of nano-TiO_2 was increased. At curing 28 days, the flexural strength was enhanced by 14, 18, 23, 25, and 27% at 1%, 2%, 3%,

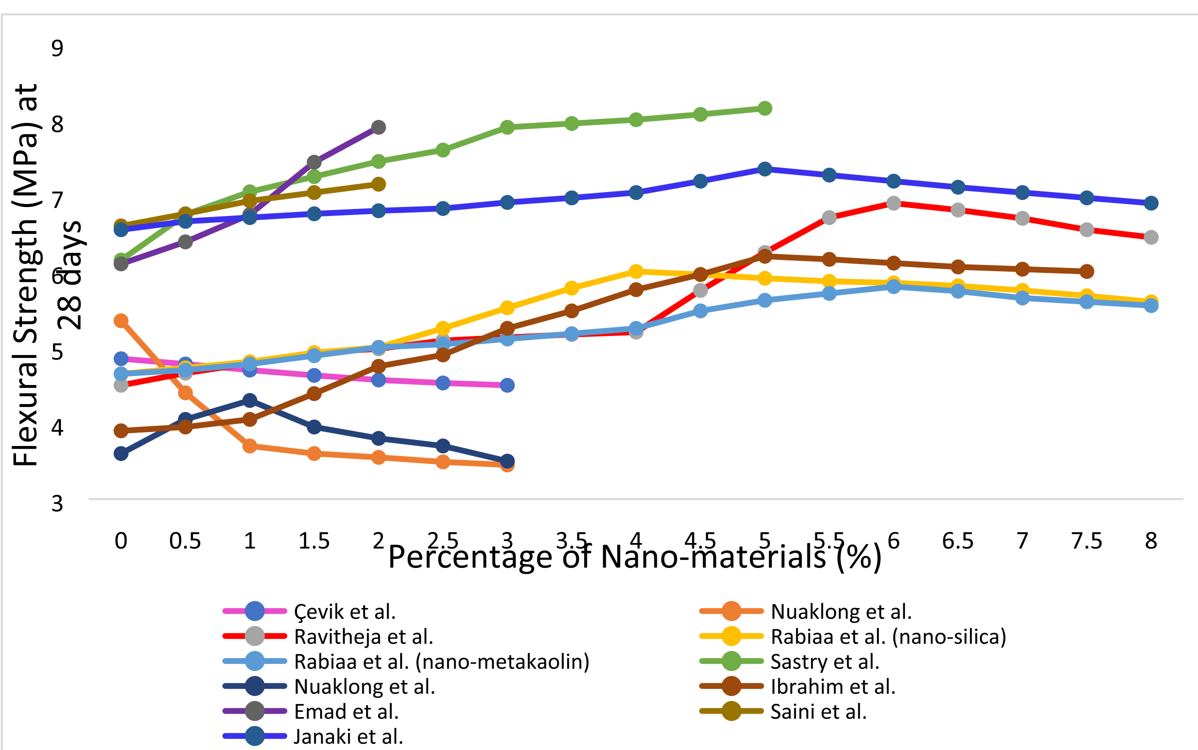

Fig. 9. Flexural strength of GPC at different percentages of NMs at the curing of 28 days.

4%, and 5% nano-TiO2 compared with the reference GPC sample with no ratio of nano-TiO_2.

Similarly, Ravitheja et al. [88] performed a research study to evaluate the influence of the inclusion of nano-clay on the mechanical characteristics of GPC. The authors noted that at the curing of 28 days, the flexural strength of GPC was increasing at the optimal dose of 6% nano-clay, and after that, the flexural strength was reduced. The highest flexural strength at 28 days was 6.9 MPa which was observed at 6% nano-clay. In comparison, the reference sample with no nano-clay had a flexural strength of 4.3 MPa on the same curing days. Janaki et al. [147] revealed that the flexural strength of GPC was enhanced when distinct amounts of carbon nano-tubes were introduced to the GPC as the flexural strength was improved by 17 and 35% at the percentage of 0.01% and 0.02% carbon nano-tubes. Compared to past research, very few scholars [19,100] revealed that adding nano-silica decreases the flexural strength of GPC. Nuaklong et al. [19] demonstrated that the flexural strength of GPC comprising 1%, 2%, and 3% of nano-silica was lesser than the samples consisting of no nano-silica. For instance, at the curing of 28 days, the flexural strength was decreased by 27, 31, and 35% at 1, 2, and 3% doses of nano-silica. The reason behind it is similar, as clarified in the split tensile strength segment. Moreover, including nano-silica raised the brittle behavior of GPC by reinforcing the ITZ amid the binder's paste and aggregate [19]. Furthermore, enhancement in flexural strength of various binder source geopolymer concrete was revealed as multiple doses of nano-calcium carbonate [101], graphene nano-platelets [92], carbon nano-tubes [133], multi-walled carbon nano-tubes [104], and nano-TiO_2 [148]were introduced to the GPC.

4. Durability characteristics of geopolymer concrete with nanomaterials

The durability of concrete materials can be defined as the ability to resist or withstand harsh conditions/surroundings when concrete is exposed to it, for example, resistance against acidic chemicals, sulfates, elevated temperature, harmful elements, etc. [149]. For this purpose, different test procedures, standardized by the regulating body, are performed to examine the durability of concrete. In this regard, to analyze and review the durability of GPC modified with various types and proportions of nanomaterials, the following tests were considered; resistance against aggressive elements, rapid chloride penetration test, sorptivity, and water absorption.

4.1. Resistance against penetration of chlorides

Researchers utilize a rapid chloride penetration test to assess the durability of GPC by observing the percentage of electric charge passing through a 100 mm diameter, 50 mm thick sample, adhering to ASTM C1202 [150] standards. A 60 V voltage is sustained throughout the test on both sides of the concrete sample. One electrode is immersed in 0.3 M sodium hydroxide, while the other is submerged in a 4% sodium chloride solution. The permeability of the concrete is qualitatively evaluated based on the electric current traversing the sample [151]. ASTM C1202 [150] classifies the concrete mixes into five categories, determined by their performance when the electric current flows through the specimens.

Most of the research showed that the value of the rapid chloride penetration test was reduced when nanomaterials were introduced to GPC. However, a significantly smaller number of studies revealed that the value of the rapid chloride penetration test of GPC was enhanced as nano-materials were introduced to the concrete mix, as presented in Fig. 10. Sastry et al. [110] conducted research to assess the impact of various doses (0%, 1%, 2%, 3%, 4%, and 5%) of inclusion of nano-TiO_2 on the mechanical and durability properties of fly-ash-based GPC. The authors revealed that the electricity traveled over the GPC samples was reduced up to 3% nano-TiO_2 compared to the reference sample, and then the traveling of electric charge was enhanced. The authors also noted that every sample of GPC had the value of rapid chloride charge passing (Coulombs) of 2000 to 4000, which is classified as moderate concrete in ASTM C 1205.

Similarly, Kotop et al. [2] studied the impact of introducing nano-clay and carbon nanotubes on the different characteristics of slag and fly-ash-based GPC. The authors revealed that including nano-clay and carbon nanotubes in the GPC enhanced the resistance against penetration of chloride in comparison with the sample mixtures of the GPC specimen. The value of the rapid chloride penetration test was reduced by 22, 25, 10.2, 13.3, 7.8 and 6.4% at the hybrid amid nano-clay and carbon nanotubes of 2.6–0.02, 2.6–0.03, 5–0.02, 5–0.03, 7.5–0.02, 7.5–0.03%, correspondingly, in comparison with the reference GPC's specimens. The authors revealed that carbon nanotubes with a uniform distribution could significantly enhance particles' densification in GPC, resulting in a very dense and firm matrix. This phenomenon arrests the spreading of cracking by averting and bridging the cracking formation, enhancing the resistance against chloride penetration. Janaki et al. [152] revealed that electric current traveling was raised as more carbon nano-tubes were introduced to the pavement made of GPC, and vale of chloride penetration was reduced as the silica fume was introduced to the same pavement made of the GPC. Adak et al. [107] revealed that the value of chloride penetration was increased as the amount of colloidal nano-silica, hybrid nano-silver, and nano-silica were introduced to the mix of the GPC. The authors claimed that more crystal elements were developed in the existence of colloidal nano-silica. As a result, the electrical current traveling was reduced and enhanced the concrete's resistance against chloride penetration. The same test outcomes were also observed by Sarkar et al. [96] and Maiti et al. [122], even though they utilized different doses and kinds of nano-materials to enhance the different characteristics of GPC. Behfarnia et al. [78] assessed the impact of the inclusion of micro and nano-silica on the permeability of GBFS-based GPC. The authors noted that the value of rapid chloride penetration was marginally reduced at a 1% dose of nano-silica; after that, it was considerably enhanced compared with the reference samples with no proportion of nano-silica. The value of chloride penetration of the reference specimen was 1932 Coulombs at the curing phase of 90 days, and this was reduced to 1872 and 1887 Coulombs at 0.5 and 1% dose of nano-silica, while the electrical current traveled was raised to 2886 and 4765 Coulombs at 3 and 5% dose of nano-silica.

4.2. Water absorption

To evaluate the water absorption of concrete, ASTM C642 [78], BS: 122 [153] is employed. These standardized test procedures are effectively utilized in the literature to evaluate the water absorption of geopolymer composite. Usually, this test is performed to assess concrete's capability to resist water penetration inside the concrete. Over the review, it was observed that numerous research works had been performed to monitor the impact of including nanomaterials on the water absorption of GPC. The test results of water absorption from the past research are presented in Fig. 11. As every kind of nanomaterial behaves as a nano-filler, it reduces the micro-pores in the matrix, including nanomaterials, considerably decreasing the percentage of water absorption in GPC up to the optimum dose. As with the strength characteristics, a dose of nano-material higher than the optimal amount was useless to improve the water absorption because of nanomaterials' poor spreading and flocculation.

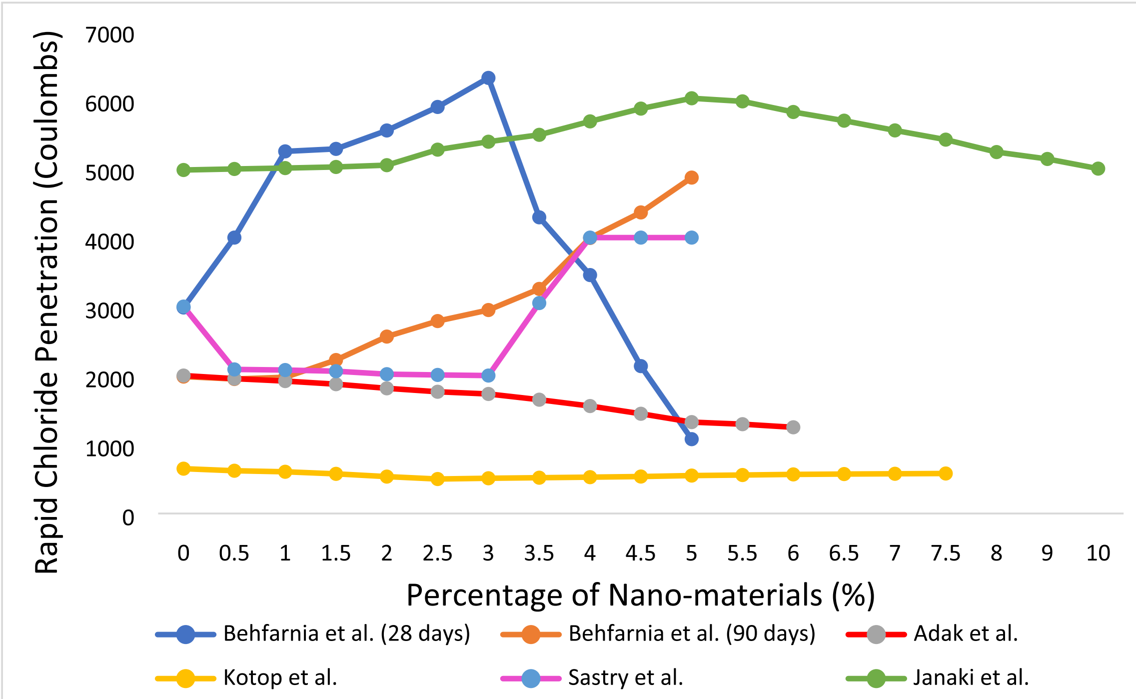

Fig. 10. Rapid chloride penetration vs. Different types and amounts of NMs in GPC.

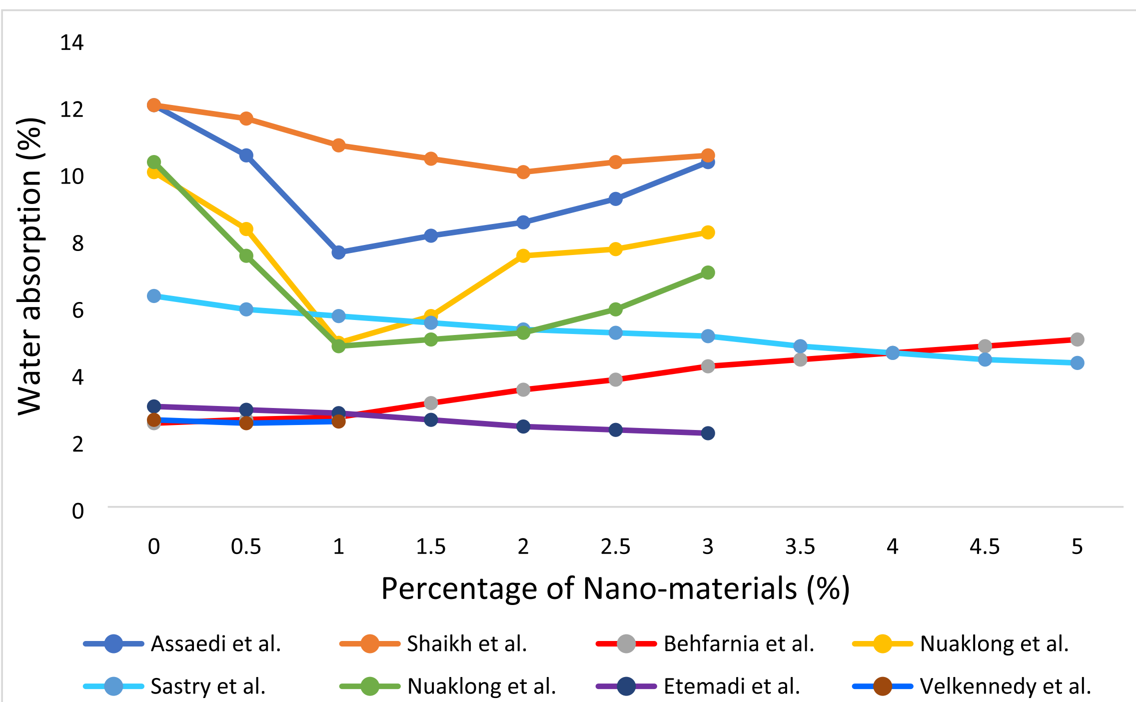

Fig. 11. Water absorption vs. Different types and amounts of NMs in GPC.

Sastry et al. [110] assessed the impact of various doses of nano-TiO_2 on the strength and durability characteristics of GPC. The authors revealed that as the dose of nano-TiO_2 was raised in the GPC, permeability, and water absorption were reduced. The water absorption was decreased by 4.08, 5.1, 9.3, 9.9, and 14.2% at 1%, 2%, 3%, 4%, and 5% nano-TiO_2 than the reference sample. This outcome can be ascribed to including nano-TiO2 in GPC, which reduced nano-voids and pores, reducing water absorption [110]. Maiti et al. [122]also claimed the same test outcome regardless of utilizing different doses of nano-TiO_2. Nuaklong et al. [127] performed research to evaluate the impact of including nano-silica on different characteristics of fly ash-based GPC with recycled aggregate. The authors reported that introducing nano-silica decreases the water absorption and porosity of GPC, as the dose of nano-silica was raised from 1 to 2, and 3% of the water absorption of GPC was raised. The water absorption was reduced by 54.8, 46.3, and 33.7% at 1%, 2%, and 3% doses of nano-silica than the reference specimen. Ekinci et al. [154] also discovered the same test results; their test outcome referred to the development of frail zones because of the incomplete spreading of nano-silica in the matrix of GPC, which most possibly happens when the proportion of nano-silica is surpassed from its optimal quantity [155], this increases the space for the permeability in the matrix of GPC, hence permitting extra water to infiltrate the GPC more effortlessly and resulting increase of water absorption.

Though Sun et al. [156] observed that water absorption was reduced by increasing the nano-silica dose, the water absorption was decreased by 12, 16, and 24% at 1%, 2%, and 3% of nano-silica was introduced to the GPC than the reference GPC. The same test results had also been observed in the literature [105,157,158] when different amounts and sorts of nano-materials were introduced to geopolymer concrete. Moreover, a research study by Velkennedy et al. [115] and Etemadi et al. [117] noted a minor enhancement in water absorption of GPC as nano-silica was introduced to the GPC. Adak et al. [87] revealed that water absorption was enhanced at a dose of 6% nano-silica, even though distinct solutions of Na $(OH)_2$ were employed. It was also noted that introducing 6% nano-silica to the GPC improved the pore structure as it was the optimal dose [159]. Furthermore, Samadi et al. [136] and Huseien et al. [137] performed a research study to assess the impact of waste glass nano-powders on the strength and durability of slag and FA-based GPC. The authors claimed that water absorption was augmented up to a dose of 10% waste glass nano-powders; the water absorption was then raised. The water absorption of GPC has reduced by 13.2% and 5.9% at 5% and 10% doses of waste glass nano-powders than the reference GPC sample. This test outcome was ascribed to developing a packed gel of calcium-alumi nate-silicate-hydrate up to 10% dose of waste glass nano-powders, enhancing the strength with less water absorption. The newly formed calcium-silicate-hydrate was filled with pores [160], and at more than 10% dose of waste glass nano-powders, porosity was increased in the GPC. There is not an adequate proportion of calcium-silicate-hydrate gel to recompense for these pores; hence water absorption was raised. Gawaad et al. [94] revealed that including multi-walled carbon nano-tubes augments slag-based GPC's water absorption at the curing stage of 90 days, while at 7 and 28 days of curing, the water absorption was augmented at 0.2% of multi-walled carbon nano-tubes and then it was raised.

The authors utilized 4 distinct doses of multi-walled carbon nanotubes (0.1%, 0.2%, 0.3%, 0.4%); the authors noted that the optimal dose of multi-walled carbon nanotubes was 0.1%. Zidi et al. [105] evaluated the impact of nano-Zinc on the strength and thermal characteristics of GPC. The authors observed that with the increase in the dose of nano-Zinc up to 0.5%, the GPC's water absorption was reduced. This outcome was ascribed to reduced pores and voids inside the GPC [161]. A detrimental effect was observed at 0.7% of nano-Zinc because of the flocculation of nano-Zinc particles in the GPC. Sanjayan et al. [162] researched the joint effect of nano-alumina and nano-silica on the water absorption of mixed fly ash and rice husk ash-based GPC; the shapeless particles of silica accelerating the process of polymerization, which resulted in the packed matrix with reduced water absorption. The nano-alumina particles were stable and contributed to the reaction of alumino-silicates and behaved as nano-fillers and decreased water absorption. Rostami et al. [78] revealed that including nano-silica resulted in an amplified longer and shorter-term water absorption capacity of slag-based GPC after assessing the impact of including micro silica and nano-silica on the permeability properties of slag-based GPC. This outcome was ascribed to the developing of a new phase in the GPC.

4.3. Resistance against aggressive surroundings

In past research, Various corrosive chemicals, including sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sulfuric acid (H_2SO_4), magnesium sulfate ($MgSO_4$), and hydrochloric acid (HCl), were used to assess the durability performance of GPC containing nano-materials. Researchers conducted standardized methods to measure the reduction in the concrete sample's weight and remaining compressive strength after subjecting the concrete to harsh environments., as presented in Fig. 12 and Fig. 13.

Çevik et al. [103] performed the study to examine the impact of introducing nano-materials on the durability against strong chemicals and strength characteristics of fly-ash-based GPC. The authors utilized 3 distinct solutions: 3.5% seawater, 5% H_2SO_4, and 5% $MgSO_4$. The authors noted that the reduction in the GPC's compressive strength with no nano-silica was 8, 16, and 31% when the samples were subjected to seawater, H_2SO_4, and $MgSO_4$, in comparison with the reference samples, which were cured at room temperature, while this loss in compressive strength was reduced to 6, 12 and 17% as 3% nano-silica was introduced to the GPC. This outcome was ascribed to the fact that nano-silica augments the GPC's microstructure. Also, the destruction of the (Si-O-Al) bridge might be the reason for the reduction of the fly ash-based GPC subjected to an acid test [163]. Çevik et al. [103] revealed that including nano-silica reduced the weight loss of ash-based GPC when subjected to different strong chemicals. Sastry et al. [110] claimed that including nano-TiO_2 enhanced the durability of fly ash-based GPC when the samples were subjected to 5% $MgSO_4$ and 5% NaCl. For example, loss in sample's weight was 0.35%, 0.343%, 0.32%, 0.28%, 0.16%, and 0.13% at 0%, 1%, 2%, 3%, 4%, and 5% doses of nano-TiO_2, when the GPC was placed in the solution of 5% NaCl for 28 days and same behavior was noted in the percentage decrease of compressive strength which was 1.49, 1.31, 1.09, 1.04, 0.99 and 0.81. The same test outcome was observed when $MgSO_4$ was utilized. When nano-TiO_2 was introduced to the GPC's sample, the proportion and size of unreacted fly ash particles reduced, resulting in quick hydration and developed products of hydration because of the nano-filling and nucleation effect. Patel et al. [109] researched to note the effect of including nano-silica on the durability and strength characteristics of GPC. The authors placed the GPC in NaCl for 28 and 56 days to consider the weight loss and compressive strength reduction. The authors noted that loss in weight and compressive strength was reduced as the molarity of NaOH was raised. In contrast, a slight reduction in weight loss and compressive strength was noted as the dose of nano-silica was raised. Mahboubi et al. [164] revealed that the durability behavior of GPC was augmented in acidic surroundings by introducing NC and NS to the GPC. The weight of reference samples was 0.85–0.95 times the primary weight when subjected to the acidic environment for 4 weeks. This weight reduction was reduced to 0.13 to 0.15 of their primary weight as nano-clay and nano-silica were introduced to the GPC. The same test outcomes have also been noted by Etemadi et al. [117] and Vyas et al. [165]. They utilized HCl, $NaSO_4$, and H_2SO_4 to evaluate the durability behavior of FA-based GPC with different doses of nano-silica.

Furthermore, Deb et al. [166] assessed the impact of introducing nano-silica against the resistance to the acid attack of GPC. After placing the samples of GPC in acid solutions for some days, the effect on the sample's microstructure, variation in weight, and compressive strength was assessed. The authors revealed that with the inclusion of 2% nano-silica, the loss in weight after placing samples for 90 days in 3% H_2SO_4 reduced from 6.5% to 2.5%. The decrease in compression strength in the specimens of GPC with no nano-silica ranged from 29% to 40%, while the loss in the sample's compressive strength with nano-silica was in the middle of 8 to 12%. This can be attributed to de-polymerizing the alumino-

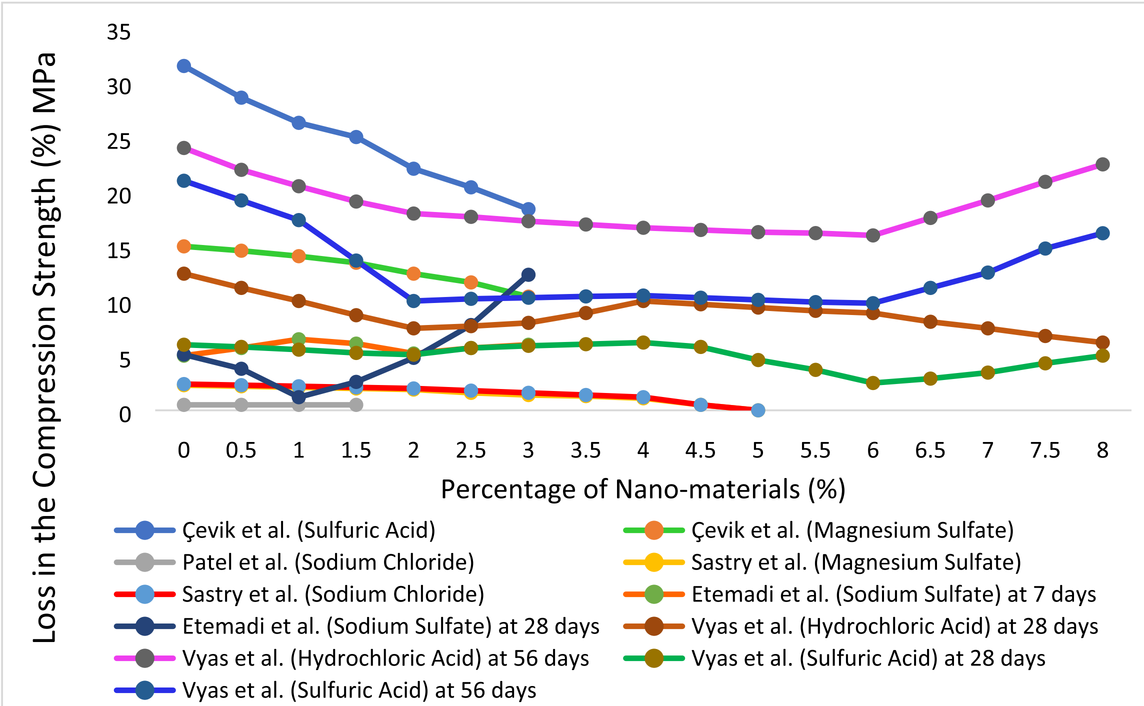

Fig. 12. Residual Compression strength vs. Different types and amounts of NMs in GPC.

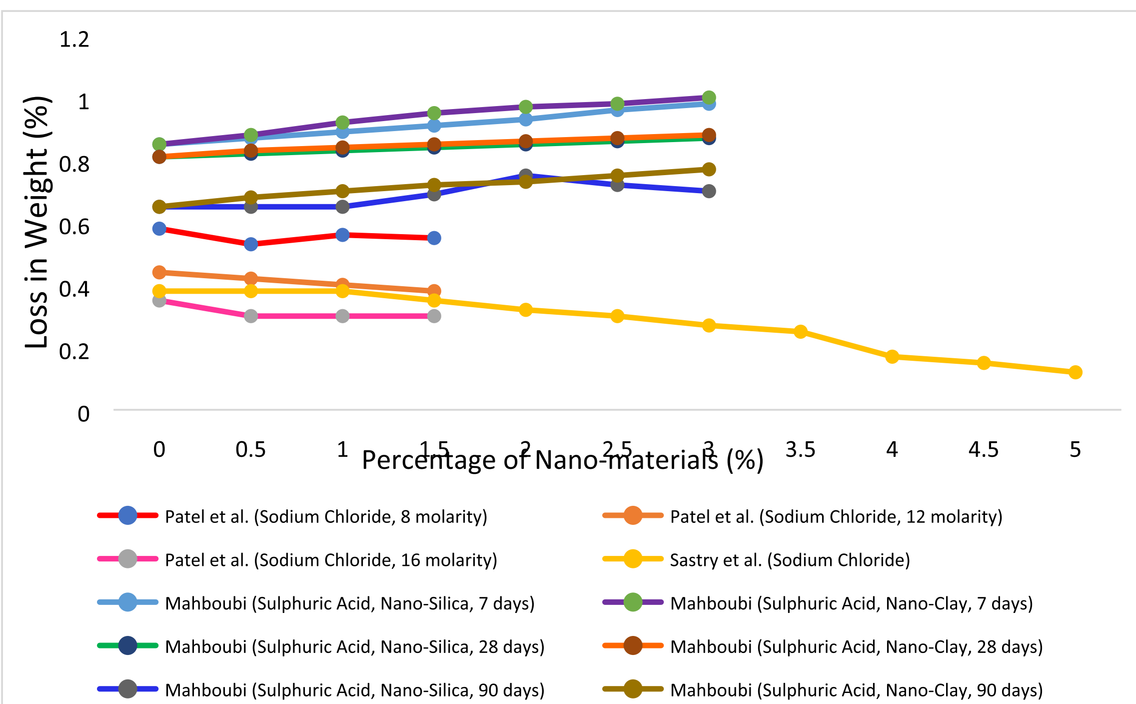

Fig. 13. Loss in Sample's Weight vs. Different types and amount of NMs in GPC.

silicates polymer in the acidic medium [167];. At the same time, including nano-materials in the GPC caused the reduction of loss in weight and compressive strength; this was ascribed to the pore improvement progression of nano-materials, which averts the channel of dangerous materials into the deep layer of the well-hydrated gel. Also, nano-materials form a dense structure that resists degradation when exposed to an acidic environment [168]; nano-silica will also augment the proportion of silica which is soluble in the mix of GPC, which results in a dense layer and decrease the extent of wear and tear of geopolymer concrete [169]. Unlike the test outcomes mentioned earlier, some researchers reported that adding nanomaterials would cause a more significant loss in the sample's weight during its exposure to acidic surroundings. Nuaklong et al. [19] reported that after 4 months of samples placed in an acid solution, the loss in weight for mixtures of geopolymer recycled aggregate concrete comprising 1, 2 and 3% nano-silica was 30, 33, and 31%, in comparison to 28% for reference specimens with no dose of nano-silica. This can be ascribed to the existence of un-reacted particles of nano-silica in the large pores, which decreases the size of space accessible for products that are formed due to expansive reaction which increases the internal pressure. This increases the decay rate and ultimately leads to wear and tear of geopolymer concrete [170,171].

4.4. Sorptivity

This test follows the standard procedure mentioned in ASTM C 1585 [172]. The sample, which is pre-dried, its rise in mass due to absorption of water by capillary in a particular way, is evaluated by this test; this is also called the sorptivity index. This is a good predictor of near-surface concrete's quality, which directs durability in terms of rusting of steel rebar inside concrete [170]. It was observed that some of the researchers performed this test to assess the GPC's durability behavior. All in all, it was noted that including nanomaterials will reduce the sorptivity value, as presented in Fig. 14.

Sastry et al. [110] performed a research study to assess the effect of introducing various doses of nano-TiO_2 on the mechanical and durability characteristics of fly ash-based GPC. The authors revealed that the sorptivity reduced with the increase in the dose of nano-TiO2. For instance, sorptivity was decreased by 12.4, 19.6, 25.2, 31.7, and 33.8% at doses of 1%, 2%, 3%, 4%, and 5% nano-TiO_2 in comparison with the control GPC's specimen. Similarly, Nuaklong et al. [127] performed a study to examine the impact of including nano-silica on different characteristics of geopolymer recycled aggregate concrete. The authors noted that the sorptivity was reduced as the nano-silica was added to the mix of GPC. The reference specimen of GPC's sorptivity was 66.5×10^{-3} mm/s$^{0.5}$, whereas this was reduced to 16.3×10^{-3} mm/s$^{0.5}$, 26.8×10^{-3} mm/s$^{0.5}$, and 38.2×10^{-3} mm/s$^{0.5}$ at 1%, 2%, and 3% nano-silica [127]. The authors also revealed that a 1% dose of nano-silica was optimal. After that dose, the inclusion of nano-silica caused a rise in the value of sorptivity for modified GPC due to the development of weak zones because of the insufficient spreading of nano-silica in the mix of GPC [127], more permeable get accommodated in the mix of concrete, which permits external water to infiltrate in the concrete's matrix. Saini et al. [146] evaluated the characteristics of slag-based geopolymer self-compacting concrete utilizing nano-silica. The samples were weighed at intermissions of 1, 6, 12, 18, 25, 50, 100, 150, 200, 250, 1500, 2750, and 4350 min, and it was noted that the inclusion of nano-silica raised the values of sorptivity for modified GPC as compared to reference GPC. Similarly, Moeini et al. [146] and Ozakça et al. [121] revealed that the sorptivity values were reduced when different doses of nano-silica were introduced to the GPC. Deb et al. [166] performed experimental work to observe the impact of including nano-silica on the resistance against acid and sorptivity index of GPC. The authors reported that for the control sample, the value of sorptivity was varied from 3.556×10^{-3} mm/s$^{0.5}$ to 3.671×10^{-3} mm/s$^{0.5}$, and for the sample with 2% nano-silica, sorptivity was reduced to the range of 1.50×10^{-3} mm/s$^{0.5}$ to 2.09×10^{-3} mm/s$^{0.5}$. The reduction in the sorptivity of GPC's specimens proves that nano-silica has decreased the permeability by the impact of nano-filling and the development of different products of the reaction of nano-silica; hence, sorptivity was reduced [166].

5. Microstructural Analysis

As said earlier, the basic process behind enhancing the GPC's performance by including various kinds of nano-materials is connected with improving concrete's microstructure. Because of the involvement in the pozzolanic reaction, the nano-materials capability of nano-filling, geo-polymerization, pore-structure, and ITZ is significantly enhanced. Transmission electron microscope [173], scan electron microscope (SEM) [133], Fourier transform

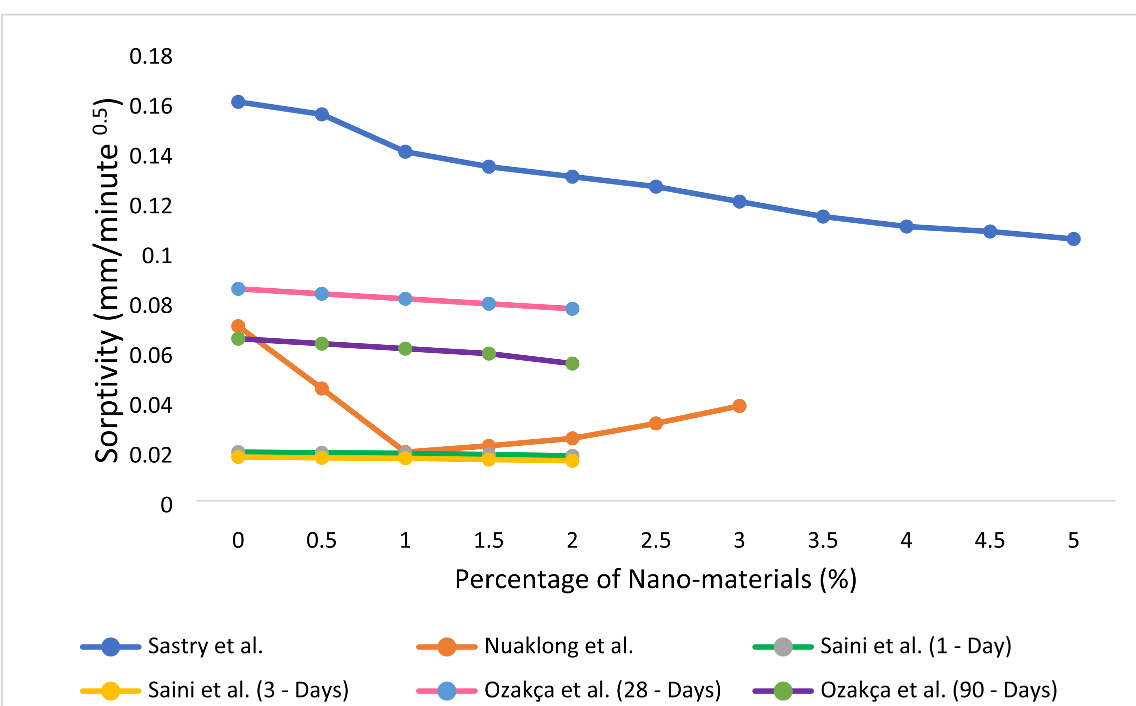

Fig. 14. Sorptivity vs. Different types and amounts of NMs in GPC.

infrared spectroscopy (FT-IR) [174], x-ray fluorescent (XRF) [175], x-ray diffraction [176] are tests and procedures through which the researchers examine the microstructure characteristics of GPC. The strength and durability properties of materials are related to the pores and voids inside the materials [177]. Generally, when GPC has low porosity, packed microstructure, and high density, it has high mechanical properties [178]. The following are the thoroughly reviewed test sections about SEM, FT-IR and XRD of the geopolymer concrete modified with different types and proportions of nanomaterials.

5.1. Scan Electron Microscope

SEM can be an effective method when analyzing GPC from the nanoscale to the micro-meter. Scan Electron Microscope utilizes a heavy magnification of up to 250 000 times to develop exact images of a broad spectrum of materials [179]. For GPC, Scan Electron Microscope was heavily utilized to examine the impact of nanomaterials on the microstructure improvement of GPC over the period by taking highly magnified photos of geopolymer concrete.

Behfarnia et al. [78] performed a microstructure study on slag-based GPC modified with nano-silica and micro-silica to evaluate the impact of adding nano-materials on the concrete's microstructure, and it was noted that the inclusion of micro-silica and nano-silica augmented the GPC's microstructure as presented in Fig. 15. This outcome was ascribed to the development of other calcium-silicate-hydrate gel because of the inclusion of nano-silica in the concrete's matrix and the pozzolanic behavior of nano-silica, which slowly fill the voids at the nano-level. This calcium-silicate-hydrate gel sticks to GPC's particles and connects them. Similarly, a research study was performed by Ibrahim et al. [111] to show the influence of the addition of nano-silica on the microstructural and mechanical properties of GPC. The GPC specimens were arranged with 0%, 1%, 2.5%, 5%, and 7.5% doses of nano-silica with a surface area of 75 m^2/g, a density of 1.3 g/cm^3, and an average particle size of 30 to 35 nm. The Scan Electron Microscope categorized the elemental arrangement and morphology of the concrete samples on the mid-portion of GPC's sample. The authors noted that including nano-silica significantly augmented the microstructure of modified concrete than the control sample with no dose of nano-silica. The authors also noted that introducing 5% of nano-silica was the optimal dose to make the GPC's microstructure dense and uniform with a low amount of un-reacted particles of nano-silica. When the 7.5% nano-silica was added, then a greater number of unreacted particles were observed, as presented in Fig. 16. This outcome was reasoned to the circumstance that the silica and alumina are the key components for the method of polymerization. The proportions of silica and alumina considerably affected the enhancement process of GPC's microstructure [180].

As a result, introducing nano-silica to the mix of GPC will cause a rise in silica components and accelerates the activation of GPC because of the chemical process of alkaline chemicals, silica, and alumina [181]. Though it was revealed that at the inclusion of 2.5% nano-silica, only fractional pore's filling was noted, whereas the flocculation of the nano-silica happened at the dose of 7.5% nano-silica; hence, the nano-silica didn't improve the microstructure as well as strength of the GPC at this high dose [113]. Mus-

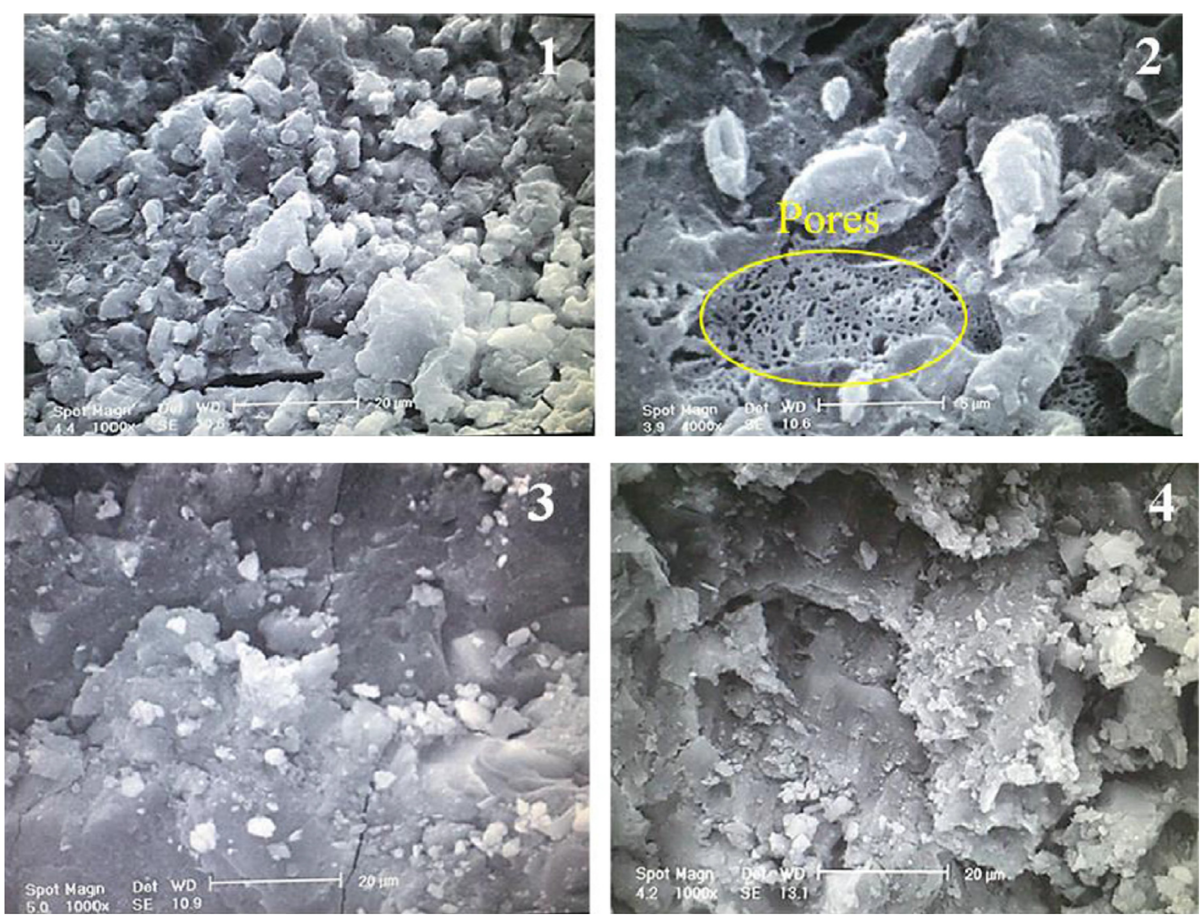

Fig. 15. Scan Electron Microscopic micrograph of (1) Reference sample at a magnification of 20 μm, (2) Reference sample at a magnification of 5 μm, (3) Specimen comprising 10% micro-silica at a magnification of 20 μm, (4) Specimen comprising 3% nano-silica at a magnification of 20 μm (Used as per Permission from Elsevier [78]).

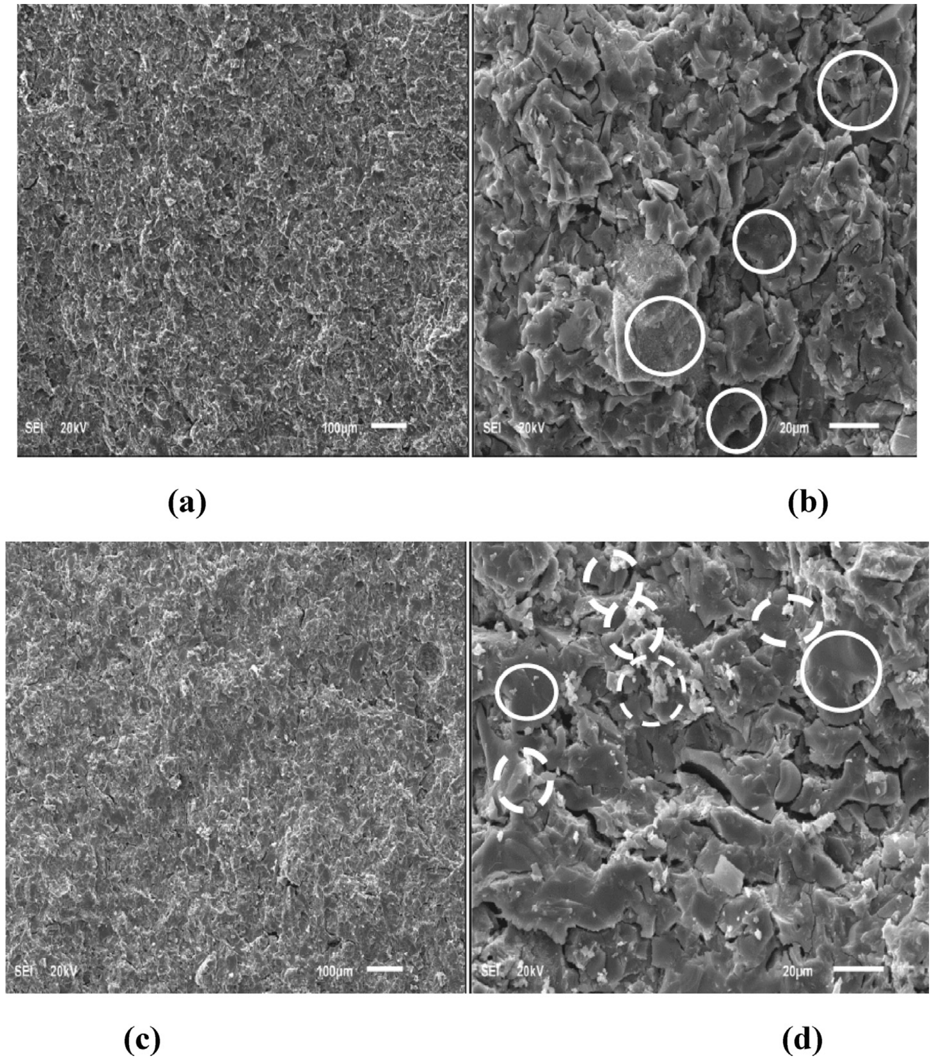

Fig. 16. Scan Electron Microscopic micrograph of (a) Alkali-activated sample with 5% nano-silica; (b) Solid circles in sample present homogeneous gel in the concrete's matrix; (c) Alkali-activated sample with 7.5% nano-silica; (d) Solid circles in sample presents homogeneous gel and dashed circle present unreacted particles in the sample's matrix (Used as per Permission from Elsevier [111]).

takim et al. [77] evaluated the impact of introducing micro-silica and nano-silica on the workability, mechanical, durability, and microstructure properties of fly ash/slag-based GPC. They noted that the inclusion of nano-silica and SF to the GPC resulted in the augmented microstructure of GPC by offering silica components which induce a high extent of poly-condensation and polymerization progression that assisted in considerable densification of the entire concrete's matrix, which results in the microstructural improvement and an enhancement in mechanical strength. Sastry et al. revealed that the inclusion of nano-titanium augmented the microstructure of FA-based GPC by offering a dense matrix and more reacted particles of fly ash, as presented in Fig. 17. This outcome was reasoned with the addition of nano-titanium, which accelerates the hydration speed and creates products of hydration because of the nano-filling and nucleation effect, which reduces the proportion and extent of un-reacted particles of fly ash [182]. Microstructural enhancement of GPC was noted even though various kinds of nano-materials were used [173,175]. Samadi et al. [136] and Huseien et al. [137] utilized the SEM method to examine the microstructural behavior of GPC. The authors revealed that the microstructure of FA/slag-based GPC was augmented with the 5% and 10% doses of WGNP. When the dose of WGNP was increased from 15% to 20%, the GPC's microstructure was less dense, and the samples had a high number of unreacted particles of WGNP, as shown in Fig. 18. Alomayri et al. [183] investigated the impact of including nano-alumina on fly ash-based geopolymer composite's strength and microstructure characteristics. The authors noted that adding up to 2% of nano-alumina caused a considerable reduction in permeability and provided a more uniform and packed microstructure to the sample than the mixes with no nano-alumina.

Though, when the amount of nano-alumina was more than 2%, the geopolymer composite began to lose its hardness, and micro-cracking and porosity increased with it; the authors' microstructural analysis also confirmed that. Moreover, on the Scan Electron Microscope photos that were analyzed by Abbasi et al. [104], multi-walled-carbon nano-tubes behaved as a bridging material in micro-cracks of MK-based GPC; hence, it provides an excellent bonding amid the GPC and the surface of multi-walled-carbon nano-tubes and as a result the GPC's strength was improved. The authors also revealed that an ample quantity of unreacted particles was present in the GPC at the curing phase of 1 week. These unre-

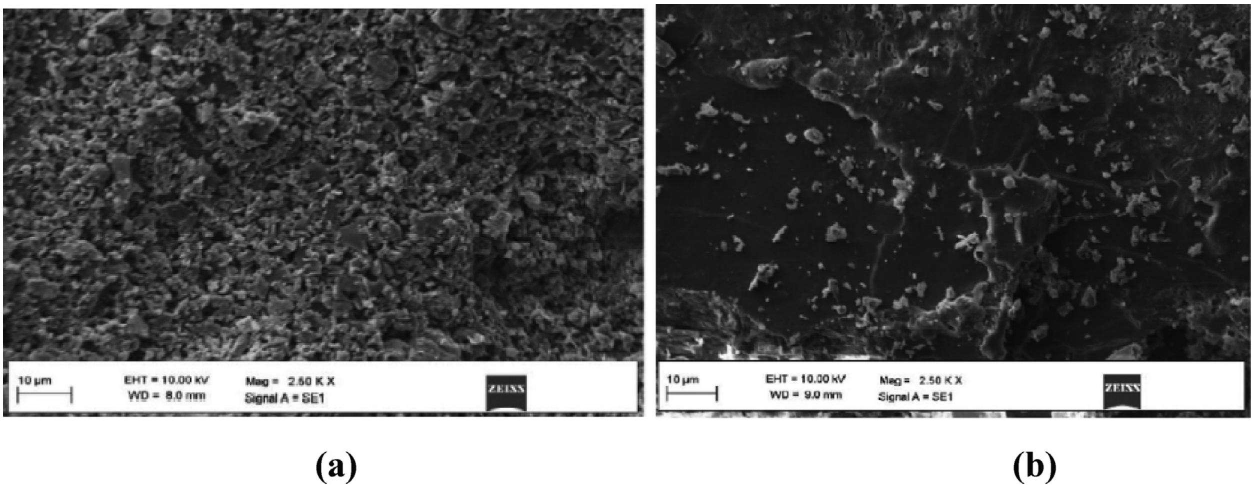

Fig. 17. Scan Electron Microscopic micrograph of (a) Reference sample, (b) Sample modified with 5% nano-titanium (Used as per Permission from Elsevier [110]).

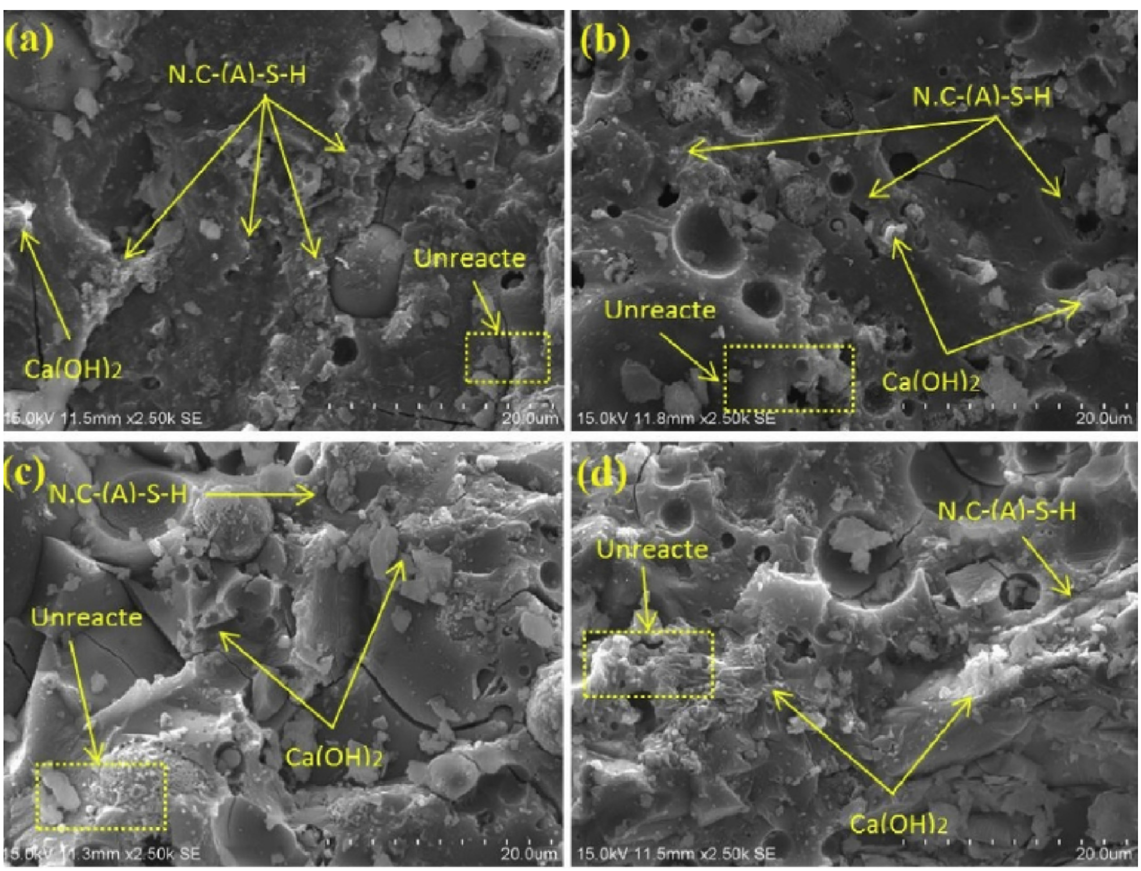

Fig. 18. Scan Electron Microscopic micrograph of sample: (a) 5% Waste-glass nano-powder; (b) 10% Waste-glass nano-powder; (c) 15% Waste-glass nano-powder; (d) 20% Waste-glass nano-powder (Used as per Permission from Elsevier [136]).

acted particles reduced considerably at the curing phase of 4 weeks because of the dissolved unreacted elements in the polymerization method. Furthermore, the authors revealed that a large proportion of pores were noted in samples that were formed due to the evaporation of water and trapped air present in the sample. In the same manner, per the scan electron microscope images, the microstructure of geopolymer concrete made from different source materials was improved by studying past papers as various doses of MK [184], nano-titanium [185], nano-silica [186], graphene nanoplatelets [92], carbon nano-tubes [70] were introduced to the samples.

5.2. Fourier Transform Infrared Spectroscopy (FT-IR)

Researchers utilize the FT-IR test to disclose the bonding data concerning the optimal composition of geopolymers and to classify the development of products of the reaction and the extent of geopolymerization in different geopolymer materials modified with nanomaterials.

Ibrahim et al. [111] performed research to evaluate the impact of introducing nano-silica on the microstructure and mechanical characteristics of natural pozzolanic materials-based GPC. The authors analyzed Fourier Transform Infrared Spectroscopy on the ground GPC from the sample's midsection. As presented in Fig. 19, the authors' outcome established that the Fourier Transform Infrared Spectroscopy analysis for the raw natural pozzolanic and GPC with no nano-silica had the same pattern. In contrast, this issue varied for the geopolymer composite incorporating nano-silica, which was reported to the development of variations in the composite. Similarly, for geopolymer composite in the presence and absence of nano-silica, a stretched vibration of the Oxygen-Hydrogen bond in the scope of 3580 to 2295 cm^{-1} and bending vibrations of Hydrogen-Oxygen-Hydrogen bond in the scope of 1525 to 1630 cm^{-1} were noted. Moreover, it was noted that the highest peaks of geopolymer composite comprised 1%, 2.5%, 5%, and 7.5% nano-silica were centered at 939, 942, 949, and 957 cm^{-1}. As the amount of nano-silica rose from 0% to 8%, the peak location in this section slowly moved to the right. Moreover, the peak raised in size as the substitution level of nano-silica rose from 0 to 7.5%, signifying that a firm geopolymer binder is developed for a high dose of nano-silica because of the high dissolution of binder source in the utilized alkali chemical [111]. In the same manner, experimental work was performed to reveal the effects of introducing nano-silica and micro-silica on the workability, microstructure, and strength characteristics of mixed FA/slag-based GPC. It was noted that the concentrated signal developed at 3493 and 3352 cm^{-1} for those samples with a dose of 1.5% nano-silica and 1.5% micro-silica, equal to the even stretched vibrations of Oxygen-Hydrogen sets observed in the molecules of water and magnesium-hydrate. Furthermore, it was determined that the development of minor bands at 2809 and 2893 cm^{-1} on the GPC with 1.5% micro-silica spectrum was ascribed to the calcium-hydrate group, signifying the existence of organic elements from the binder source material of FA.

In contrast, the band between 1641 and 1789 cm^{-1} was also ascribed to stretched and bend vibration of the Oxygen-Hydrogen bond, implying water molecules in the GPC system. The division of absorption groups in the scope of 1451 to 1482 cm^{-1} and 1419 to 1479 cm^{-1} noted on the specimens of GPC with the dose of 1.5% nano-silica and 1.5% micro-silica were ascribed to the stretching of C-O bands resulted by the un- reacted sodium positive ions and reacting with the carbon dioxide during the reaction of geo-polymerization [111]. Moreover, scholars have shown the influence of WGNP on the different characteristics of GPC. The authors revealed that Fourier Transform Infrared Spectroscopy noticed the reaction regions of Al-O and Si-O in the GPC over the chemical procedures to explore the functional groups founded on bond vibrations. Silica - Oxygen - Alumina band at 0% waste-glass nano-powder (991.4 cm^{-1}) then moved to 986.5 cm^{-1} and 988.1 cm^{-1} for geopolymer composite comprising 5% waste-glass nano-powder and 10% waste-glass nano-powder. The frequency for the Silica - Oxygen - Alumina band was reduced, signifying a rise in the gel product of Calcium (Nitrogen) – Alumina – Silica – Hydrate. This led to a uniform system for the sample comprising 5% waste-glass nano-powder and 10% waste-glass nano-powder and also reorganized the silica elements when contrasted with the samples comprising 0% waste-glass nano-powder. Increasing the proportion of waste-glass nano-powder from 15 to 20% led to a reduction in compression strength and a rise in the frequency of band values to 991.3 cm^{-1} and 996.2 cm^{-1}. The bent shapes of Silica – Oxygen – Silica at 776.4 cm^{-1} were moved to 755.6 cm^{-1} by raising the concentration of waste-glass nano-powder from 0 to 5%. This reduction in the frequency bonding of Silica – Oxygen – Silica with raising the level of waste-glass nano-powder signified a rise in the development of gel products of Calcium – Silicate – Hydrate. Raising the molecular mass of the adhered elements reduced the frequency of vibrations. Hence, the slag released solvable Calcium and displaced elements of Silica from the bond of Silica – Oxygen, which reduced the frequency of vibrations. The inclusion of waste-glass nano-powder raised the ratio of Silica/Alumina and the frequency of vibration for Silicon – Oxygen – Silica [136].

Similarly, a research study has shown the impact of introducing multi-walled carbon nanotubes on the characteristics of GPC. Their Fourier Transform Infrared Spectroscopy outcome for the GPC's sample with no multi-walled carbon nano-tubes at curing phases of 7, 28, and 90 days is presented in Fig. 20 (a). The descriptions

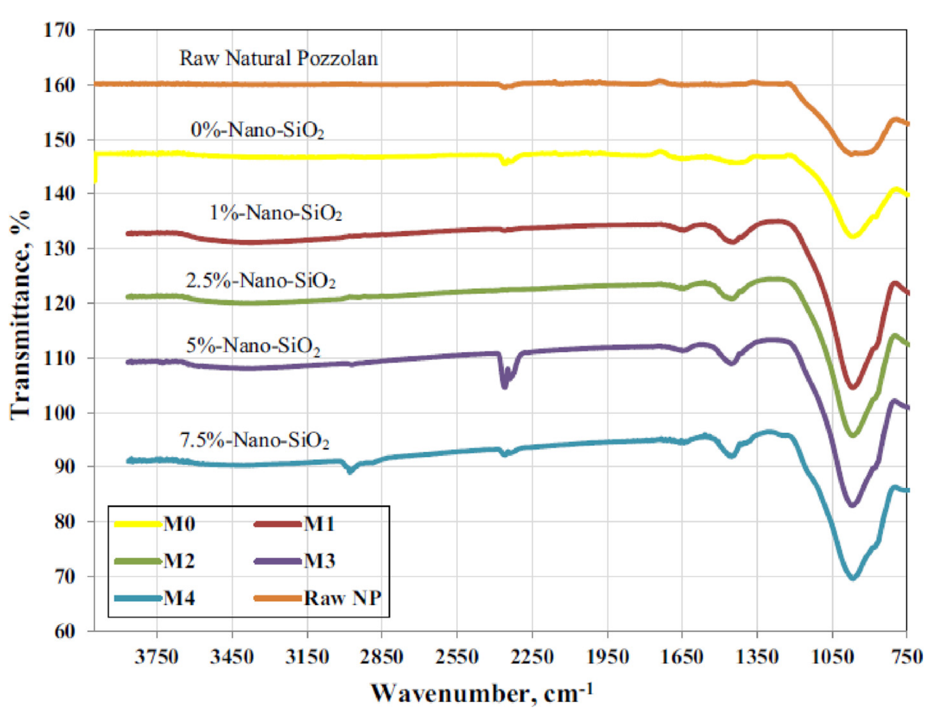

Fig. 19. Fourier Transform Infrared Spectroscopy analysis of samples formed with various amounts of nano-silica (Used as per Permission from Elsevier [111]).

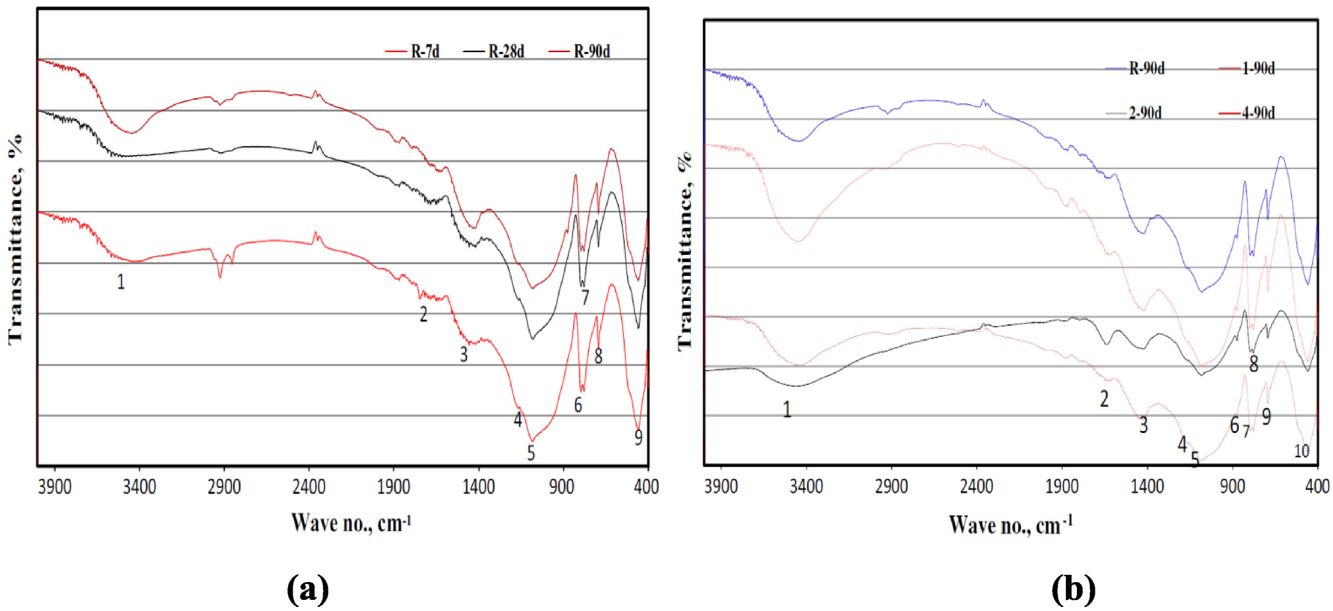

Fig. 20. Fourier Transform Infrared Spectroscopy analysis of samples (a) With no Multi-walled carbon nano-tubes, (b) With Multi-walled carbon nano-tubes (Used as per Permission from Elsevier [94]).

in Fig. 20 (b) were revealed as (1) Stretched vibration for the bonding of Oxygen – Hydrogen, (2) bent vibration of Hydrogen – Oxygen – Hydrogen, (3) stretched vibration of carbon dioxide, (4) irregular stretched vibration of Silica – Oxygen – Silica, (5) irregular stretched vibration of Silica or Alumina – Oxygen – Silica, (6) regular stretched vibration of Silica – Oxygen – Silica bond ascribed to quartz, (7) regular stretched vibration of Alumina – Oxygen – Silica, (8) regular stretched vibration Silica – Oxygen – Silica, and (9) bent vibration of Silica – Oxygen – Silica and (10) bent vibration of Silica – Oxygen – Silica [94]. The aforementioned groups were taken as follows; stretched vibrations of Oxygen – Hydrogen bonding at around 3428 and 1586 cm^{-1}, stretched vibration of carbon dioxide at around 1408 cm^{-1}, irregular stretched vibration of Silica – Oxygen – Silica bond related with the non-solubilized elements at around 1086 cm^{-1}, and irregular stretched vibration of Silica or Alumina – Oxygen – Silica related with the non-solubilized elements at around 981 cm^{-1}, carbon dioxide has irregular stretched vibrations at around 867 cm^{-1}, Silica – Oxygen – Silica bond has irregular stretched vibration at around 791 cm^{-1}, Alumina – Oxygen – Silica has a regular vibration at around 781 cm^{-1}, Silica – Oxygen – Silica has irregular stretched vibrations at around 681–700 cm^{-1}, and (Oxygen – Silica – Oxygen and Silica – Oxygen – Silica) has a bent vibration at around 428–441 cm^{-1} [94]. Lastly, Sun et al. [156] research the behavior of nano-silica on the efflorescence performance of MK-based GPC. As presented in Fig. 21, it was established that the firm peak at around 3338 cm^{-1} and 1648 cm^{-1} paralleled the stretched and bent bond of the Oxygen – Hydrogen, signifying the existence of weak bond of hydrogen di-oxide resulting from the water absorption on the surface structure. The peak at 1392 cm^{-1} was ascribed to the irregular stretched bonding of Oxygen – Carbon – Oxygen resulting from the alkali hydroxides that reacted with the outside carbon dioxide. The peak at 437 cm^{-1} was ascribed to the bent vibrational plane of Silica – Oxygen – Silica, signifying the alumino-silicates structure's development. Silica – Oxygen – Silica or Alumina's absorption peaks were noted in the sample at the peak of 994 cm^{-1} to 1048 cm^{-1} and in the MK at 1095 cm^{-1}.

The sample's Silica – Oxygen – Titanium peak could be utilized to evaluate the extent of geo-polymerization, as it was more significant than the bent peak of Silica – Oxygen – Silica [156]. Samadi et al. [136] performed FT-IR spectroscopy on the alkali-activated geopolymer material modified with the different percentages of bottle glass waste-nano powders (BGWNP), as presented in Fig. 22. The reaction site of Al-O and Si-O in the mix of alkali-activated geopolymer material was recognized by Fourier Transform Infrared Spectroscopy through chemical investigation, which enables the identification of functional bands on the base of bonded vibration. New minerals are obtained from the enhancement of base material with the dissolution of alkali chemicals, which develop compression strength in the material's matrix.

6. Sustainability challenges relevant to the current topic and recommendations for future research

This section discusses requirements for future research, drawbacks, present hindrances, and challenges noted in past studies. A large Empirical and field study is needed to gather extensive information on the durability and engineering characteristics of geopolymer composites modified with nanomaterials in different environmental conditions and prepare it according to the specific use and needs for industry practice in the construction sector [187]. Based on existing studies, it was noted that many studies have been performed on the impact of substituting or introducing nanomaterials in different geopolymers. As presented in Fig. 23, a considerable proportion of studies have been performed on geopolymer-paste (GP) comprising different kinds of nanomaterials, which accounts for nearly 51.2% of the entire literature, in comparison with the low proportion of studies performed on geopolymer mortar and geopolymer concrete, which accounts for 18.7% and 30.1% of entire study correspondingly. Hence, it is recommended to perform further studies on the engineering characteristics of GPC with nanomaterials. Per Fig. 24, the scholars have employed fly ash and slag as the main binder source material in their past study, and the 3rd most used material is MK. Though, there is low utilization of a broad range of available ashes that are pozzolanic, for instance, wheat straw ash (WSA), palm oil fuel ash (POFA), rice husk ash (RHA), bagasse ash, waste wood ash, etc. Hence, it is essential to study these waste pozzolanic materials'

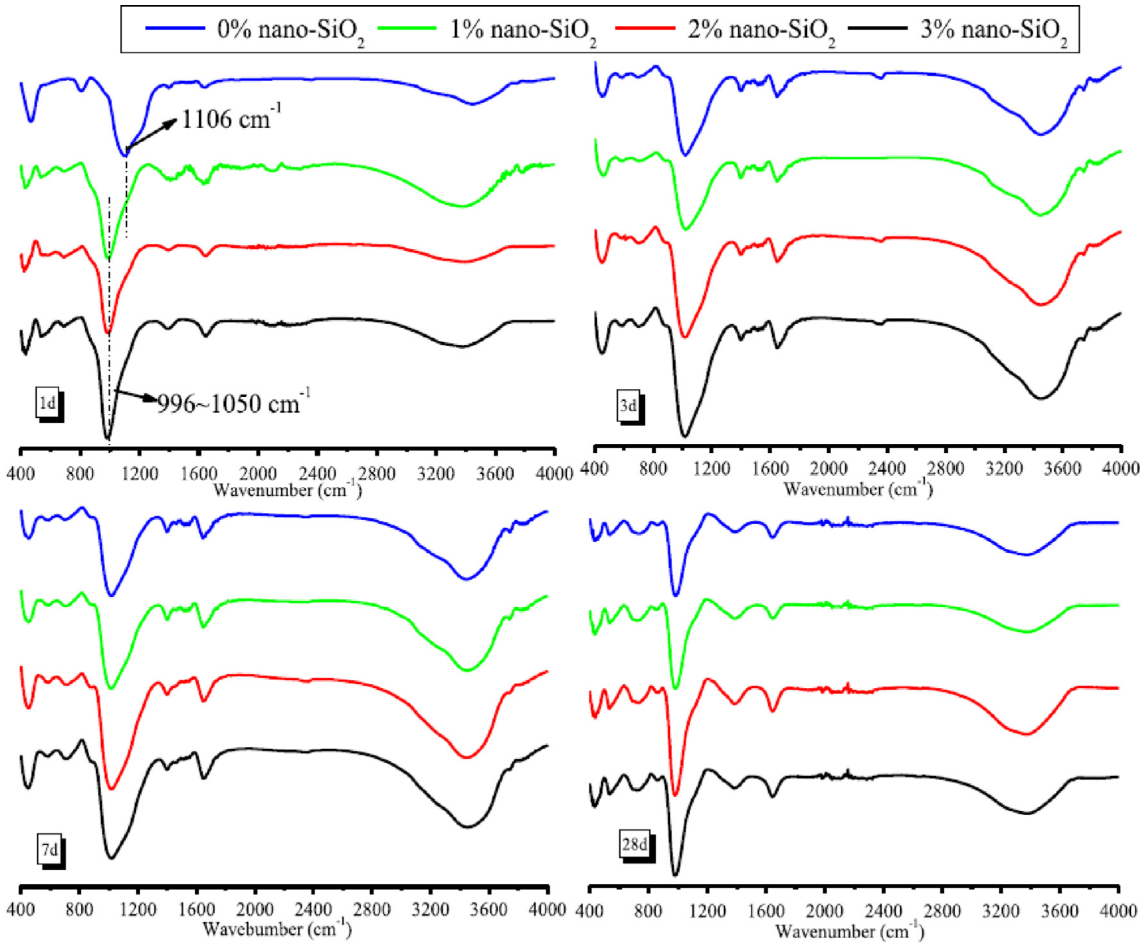

Fig. 21. Fourier Transform Infrared Spectroscopy analysis of samples with various amounts of nano-silica at the curing under room temperature (Used as per Permission from Elsevier [156]).

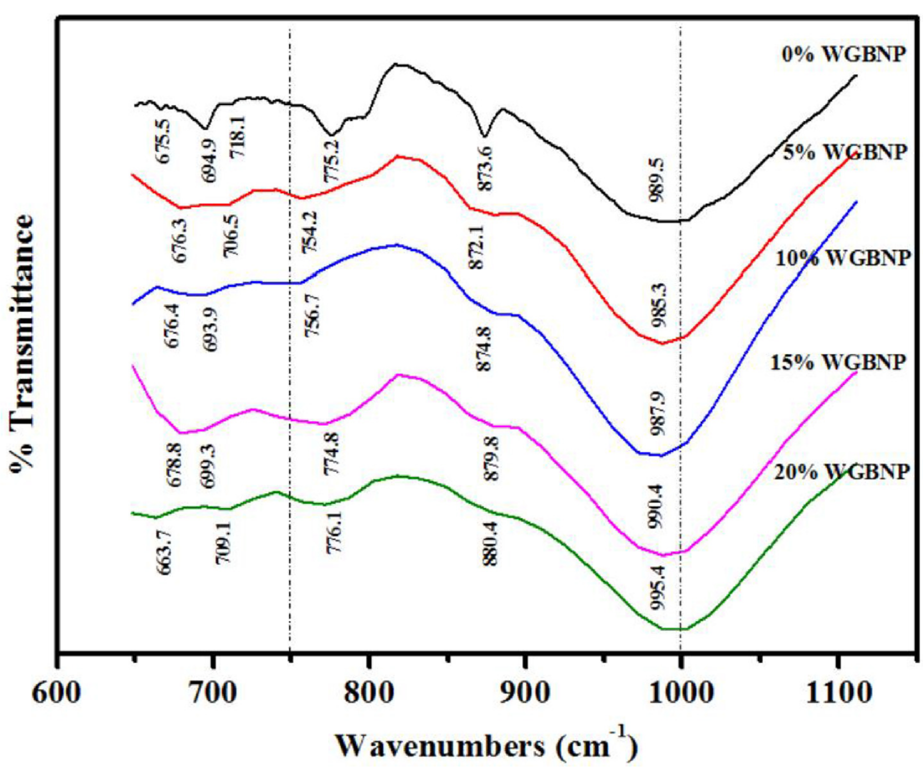

Fig. 22. FT-IR Spectroscopy of alkali-activated geopolymer material developed with different percentages of BGWNP (Used as Open). Source [136]

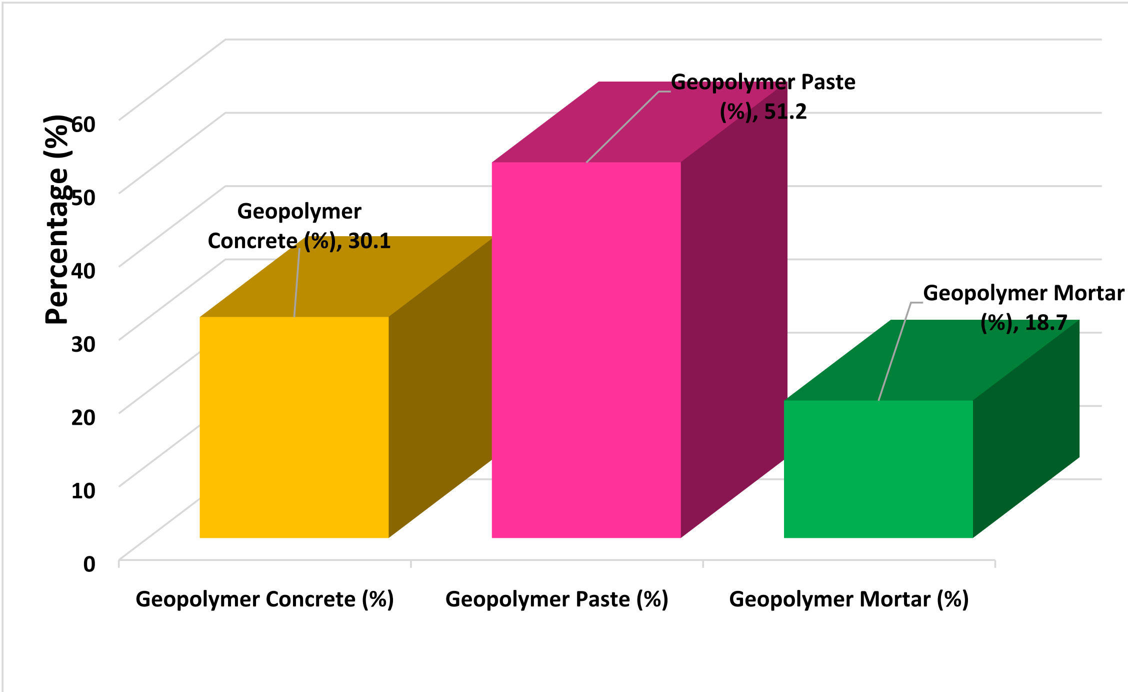

Fig. 23. Percentages of Geopolymer composites incorporated in past articles based on various doses and kinds of nanomaterials (Data from references [76,98,101,194–198]).

ashes to include them in the development process of geopolymer composites to make the product eco-friendly [188–191].

Furthermore, a meager quantity of research has focused on the synthesis process of nanomaterials from pozzolanic waste materials. Hence, more study in this domain is important for making low-cost and eco-friendly nanomaterials. Some scholars have suggested a few changes to geopolymer concrete's current conventional mix design process. Further study is needed to develop an optimized mixing proportion and mixing design for nano-modified geopolymer materials; hence, the specification of GPC as per the performance and standardization of test procedures are important to study areas that necessitate further research work. Geopolymerization is a very complex chemical procedure that researchers are continuously learning [192]. Consequently, further study on nano-modified GPC is suggested to understand the geopolymerization method better. Furthermore, one of the main challenges is certifying the level of nano-modifications in the spreading of nanomaterials in GPC; hence, further study is required to examine well and characterize the spreading of nanomaterials in GPC to attain better spreading of nano-materials. Limited studies have shown that nanomaterials spread easily in GPC with no flocculation. There is a lack of studies on examining the sustainability of the life cycle of GPC modified with nanomaterials for all the three components of sustainability, environment, social and economic perspective; hence, research about this topic is needed to examine the sustainability of nano-modified GPC thoroughly, and for this life-cycle assessment (LCA) of nano-modified GPC is necessary.

Nonetheless, the cost of nanomaterials is considered a considerable drawback for using nano-materials in the GPC [193]. The direct cost of nano-modified geopolymer composite is high despite its long-term advantage. Due to the complexity of the apparatus required to develop and classify the nanomaterials, the cost of apparatus and geopolymer technology is comparatively costly. Prices are likely to reduce as the technology related to developing geopolymers increases, then the demand will be high, and the rate will be low [191]. One drawback is the broad usage of nanomaterials in the construction sector is connected with the environment and health. Leaking of nanomaterials into the water, which outflows into the atmosphere over the formation of dust, and contact with possibly hazardous elements during construction is a serious problem that could happen. Hence, the construction sector could focus more on developing mass-scale nano-silica to be employed in the GPC. Manufacturing of Nano-silica needs low energy and a low budget to be formed, as it has a high pozzolanic behavior and nano-filing impact to form durable geopolymer material. Because the inclusion of nanomaterials considerably enhances the durability and strength characteristics of GPC, it is very suggested to include these nano-materials into geopolymer materials with low durability and strength characteristics, for instance, GPC comprising rubber pieces as coarse aggregates and GPC containing recycled aggregate, to improve the mix of the concrete. Furthermore, the behavior of GPC modified with nanomaterials exposed to high temperatures needs more research studies as a limited number of studies are available on such topics. Lastly, for the geopolymer composites (concrete, mortar, and paste) to be commercially utilized in the construction sector, the assessment related to geopolymer materials' behavior under different conditions such as bending, torsion, and twisting first needs to be evaluated in detail.

7. Conclusions

Per the comprehensive study, the process of the effect of different kinds of nanomaterials on the engineering characteristics of GPC, which includes strength, durability, and microstructure properties, is offered and conferred thoroughly. After performing a detailed systematic review of the past papers, the following points are to be made:

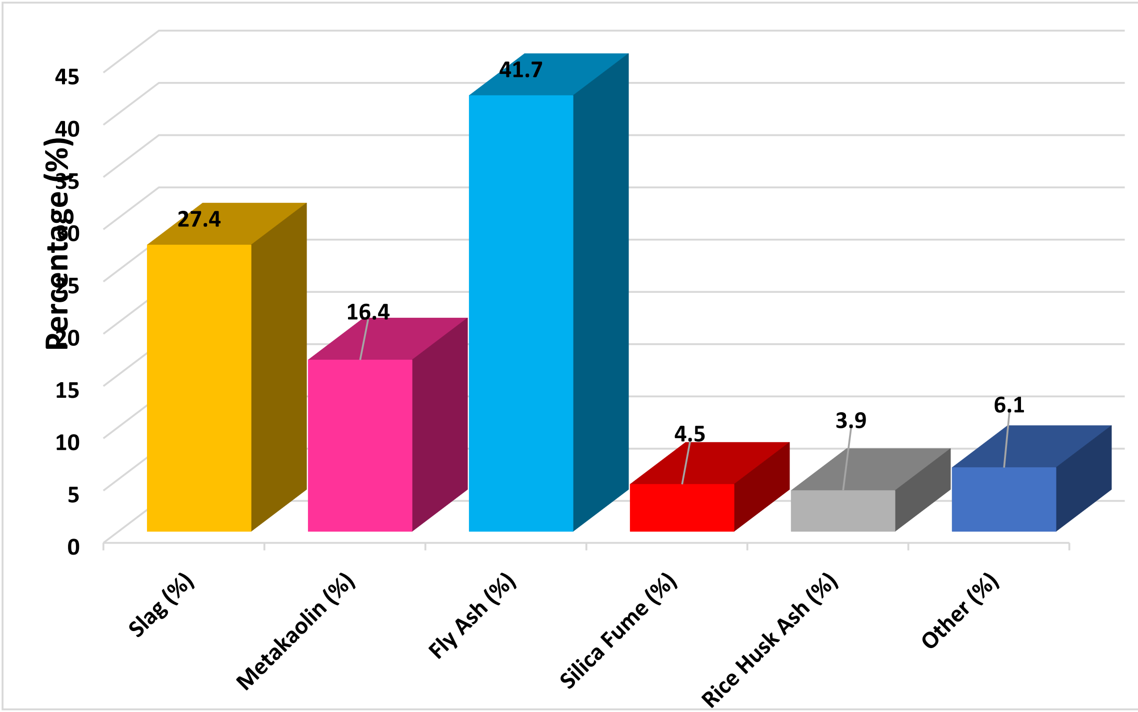

Fig. 24. Percentages of various binder source materials for the development of nano-modified GPC (Data from references [92,102–104,199]).

1. NS, NA, CNT, MWCNT, NZn, NT, NCC, NMK, NGP, and GNP are nanomaterials used in GPC, often replacing binders at less than 6%. Nano-silica (NS) is popular due to its low cost, acting as a filler, and promoting CSH gel formation, improving GPC microstructure. On average, 12.1 kg/m3, or around 4% of binder content, is replaced with nano-silica.
2. Nanomaterials (NMs) in GPC have unique effects based on their chemical and physical properties. They fill nano-level voids, accelerate reactions, participate in pozzolanic action, and enhance the ITZ. Strength characteristics, such as compressive, flexural, and split tensile strengths, increase with NM dosages up to an optimal level (2–4%). Durability also improves with various NM dosages, as they refine pores, prevent harmful materials from entering, and densify the structure, providing better resistance against external elements.
3. Nanomaterials significantly impact GPC's microstructure. SEM analysis reveals enhanced microstructure due to additional calcium-aluminate-silicate-hydrate, calcium-silicate-hydrate, and nitrogen-aluminate-silicate-hydrate gels filling nano-level pores. Nanomaterials also accelerate hydration and reduce unreacted binder material. FTIR analysis shows the development of oxygen-hydrogen, silica-oxygen-silica, and alumina-oxygen-silica bonds in GPC, both with and without nanomaterials.

8. Prospect of further research on GPC reinforced with nano-materials

The prospect of future research on geopolymer concrete (GPC) reinforced with different nano-materials is vast and promising, as it can revolutionize the construction industry and create more sustainable, high-performance materials. Here is a detailed list of research directions in this area:

1. **Nanoparticle dispersion:** Investigating methods to achieve uniform dispersion of nanoparticles within the GPC matrix to optimize their reinforcing effects and minimize agglomeration.
2. **Nanoscale reinforcement:** Evaluating the mechanical properties and performance of ultra-high-performance GPC reinforced with various nano-materials, such as carbon nanotubes (CNTs), graphene, nano-silica, nano-alumina, and nano-TiO_2.
3. **Synergistic effects:** Studying the combined impact of different nano-materials on the performance of GPC to develop hybrid nano-reinforced composites with superior properties.
4. **Durability and long-term performance:** Assessing the impact of nano-material reinforcement on the durability, weather resistance, and long-term performance of GPC in various environmental conditions.
5. **Microstructure characterization:** Employing advanced microscopic and spectroscopic techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR) to investigate the microstructural changes and chemical interactions in GPC induced by nano-material reinforcement.
6. **Rheology and workability:** Evaluating the influence of nano-material reinforcement on the rheological properties and workability of fresh GPC and developing strategies to optimize these characteristics.
7. **Self-healing and self-sensing capabilities:** Exploring the potential of nano-reinforced GPC for self-healing and self-sensing properties could lead to developing smart, resilient infrastructure systems.
8. **Life-cycle assessment and environmental impact:** Conduct comprehensive life-cycle assessments of nano-reinforced GPC to quantify its environmental benefits and potential drawbacks compared to conventional concrete.
9. **Scalability and cost-effectiveness:** Investigating methods for large-scale production of nano-reinforced GPC, addressing challenges related to the availability, cost, and processing of nano-materials.

10. **Building code development and standardization:** Collaborating with regulatory agencies and industry stakeholders to establish performance criteria, testing methods, and design guidelines for nano-reinforced GPC, paving the way for its widespread adoption in the construction industry.

By exploring these research directions, developing nano-reinforced geopolymer concrete can transform the construction sector, leading to more sustainable, durable, and high-performance materials for various applications.

Data accessibility statement

Data can be provided by demand from the corresponding author.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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