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An Investigation of the Fresh and Hardened Properties of Nano Zinc Oxide Reinforced 3D Printed Geopolymer Mortars

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Abstract
It is well known that even small amounts of nanomaterials can improve the mortar structure and enhance its fresh state and hardened properties. This paper investigates the fresh state and hardened properties of nano zinc oxide-reinforced 3D-printed geopolymer mortars. The mechanical properties of 7, 28, 90, and 180 days of 3D-printed geopolymer mortars cured at ambient temperature were investigated. For this purpose, 3D-printed geopolymer mortar samples containing 0%, 0.25%, 0.50%, and 0.75% nano zinc oxide were produced. Flow table and buildability tests were applied to these samples to determine the fresh state properties. Ultrasonic pulse velocity, flexural strength, and compressive strength tests were applied to the hardened 3D-printed geopolymer mortar samples. The best mechanical test results were obtained from 3D-printed geopolymer mortar samples containing 0.5% nano zinc oxide at the end of all curing times. In the ZN 50 series cured for 28 days, approximately 29% higher strength was obtained in FS and 66% higher in compressive strength compared to the ZN 0 series without nanomaterials. It has been noted that incorporating a tiny quantity of nano zinc oxide into 3D-printed geopolymer mortars improves their mechanical performance.

1. Introduction

Concrete is the most commonly used building material in the world, especially in the construction sector. One of the most commonly used materials in building structures is mortar. Mortar is obtained by mixing binders such as sand and cement with water. Mortar and concrete are the second most consumed materials in the world after water. One of the main industries that produce greenhouse gases is the cement industry. This cement production has a large carbon footprint and has grown to be a major source of pollution worldwide in recent decades [1].

Geopolymer (GP) is inorganic polymeric binder materials, first developed by Davidovits in the 1970s [2]. GP is an aluminum and silicate type binder material formed by activating natural and waste pozzolanic materials with various alkaline activators [3]. GPs are highly acknowledged in the concrete industry as superior cement alternatives, providing an environmentally benign and sustainable building solution. GP composites are environmentally friendly because they are sustainable, use waste materials, and do not contain Portland cement. GP mortar or concrete is known as environmentally friendly mortar or environmentally friendly concrete because it uses one or more components that are considered industrial waste materials with pozzolanic quality and limited landfill areas during production. GP mortars and concretes, can be produced by activating one or more of the following materials with alkali activators: industrial wastes such as fly ash (FA), rice husk ash, silica fume, ground granulated blast furnace slag, fired clays and shales, heat-treated materials such as metakaolin (MK), natural pozzolans such as volcanic ashes, trass, and diatomite soils, pumice, which is a type of volcanic glassy rock and also known as pumice stone, and ground perlite, which is a volcanic rock [4].

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Three-dimensional printing technology (3DPT), which has a very widespread use, has also found a place in the construction sector. The first inventor of 3DPT C. Hull, received his patent in 1986 and has shown considerable development and progress to this day [5]. With global warming and the deterioration of the ecological balance, which are among the biggest problems in the world, solutions have been sought in the construction sector for environmentally friendly production techniques, and innovative methods have been developed thanks to the opportunities provided by technological developments [6], [7]. One of these is the start of production with 3DPT. With 3D printing, a three-dimensional object modeled in a computer environment is divided into layers, and during the production phase, each layer is built on top of the previous layer and maintains its shape. Despite its high cost and complex structure, it has become widespread enough to be used in almost every field today compared to the period when it was first produced. So much so that even products that cannot be produced with classical manufacturing methods can be easily produced with 3D printers [8].

It is imperative to apply sophisticated techniques to improve the structural performance of GP mortars by adding nanomaterials. Nanomaterials have gained importance in the building sector as a way to enhance mortar performance. It has been found that the structural performance and lifespan of GP mortars can be greatly enhanced by the addition of tiny amounts of nanomaterials [1]. Many properties vary according to the different nanomaterials used. Nanomaterials are added to GP mortars to improve their mechanical properties. Theoretically, all materials in the aluminosilicate class can be activated by alkali activators and exhibit binding properties. It is known from the literature that nanomaterials added to very small amounts of alkali activators increase the mechanical performances of GP mortars [9]. The use of nanomaterials in three dimensional printed geopolimer (3DGP) mortar and concrete samples has increased recently [10]–[17]. Nano zinc oxide (n-ZN) is a promising nanomaterial because of its good semiconductor capabilities, and its ability to improve microstructure by acting as a filler and increasing mechanical strength [18]. It is also easy and economical to produce and safe for the environment [19]. However, the use of n-ZN in GP mortar samples is limited [18], [20]–[24]. Also, the use of n-ZN in 3DGP mortar samples is very limited [25]. More researchers have been examining the mechanical strength and durability properties of GP composites utilizing n-ZN in recent years [26], [27]. It is known from the literature that n-ZN has an improving effect on mechanical performance [9]. In their investigation, Raj et al. [28] found that n-ZN containing GP composites had a greater mechanical strength than GP composites. The fire resistance of plywood coated with a GP containing n-ZN was investigated by Wang et al [29]. They discovered that a flame is not necessary when utilizing huge volumes of n-ZN. Slag-based GPs were compared to n-ZN, nano-iron, and hybrid nanomaterials in terms of their physical characteristics, mechanical strength, and radiation shielding capabilities by Mohsen et al [30]. Comparing the hybrid nanomaterial series against the n-ZN series, they discovered that the hybrid nanomaterial series produced superior results in mechanical strength and radiation protection qualities. Seloglu et al. [9] compared the mechanical strength of different nanomaterials in MK-FA-based GP mortars. They found that the best results were obtained in the GP mortar series containing 0.5% n-ZN that were cured at ambient temperature for 7 and 28 days. Zidi et al.'s investigation [19] looked at how nano alumina, n-ZN, and nano silica affected the mechanical characteristics of GP composites. They stated that using n-ZN to get outcomes that were both cost-effective and highly strength. Tan et al.'s investigation [31] examined how n-ZN affected the slag-based GP's engineering characteristics. They stated that the mechanical qualities of the composite were reduced when the percentage exceeded 2%. Tanyildizi, et al. [25] investigated the effects of using n-ZN in 3DGP mortars on mechanical and durability effects. They found that the highest mechanical properties were obtained from samples containing %0.5 n-ZN.

In this experimental study, fresh and hardened properties of n-ZN reinforced FA-MK-based 3DGP mortar samples were investigated. Within the scope of the study, four different n-ZN reinforced 3DGP mortars were produced and added to the composite by volume at 0%, 0.25%, 0.50%, and 0.75% ratios. For the fresh state properties of 3DGP mortar samples, the mini-slump spread test and buildability test, which is an important test in 3D printing, were performed. To examine the hardened properties, Ultrasonic pulse velocity (UPV), flexural strength (FS), and compressive strength (CS) tests were performed by the relevant standards. The study aims to investigate the rheological and mechanical properties of 3DGP mortars produced without molds and without using cement as a binder by curing at ambient temperatures for 7, 28, 90, and 180 days. The result of this research will be helpful to structural designers who want to build sustainable 3DGP mortar.

2. Materials and Method

2.1. Materials

In the current study, FA and MK were employed as binders. Table 1 presents the properties and composition of binder materials.

To manufacture the geopolymer (GP) mortar, a binary activator consisting of Na_2SiO_3 (SM) and NaOH (SH) solution was used. The SH pellets were dissolved in water and added to the SM before the creation of the GP mortars. This process began 24 hours before the production of the GP mortar to ensure the development of a 12 M alkaline solution. Fine river Palu sand was added to this mix as an aggregate. Table 2 presents the properties of aggregate.

MK requires extra water in the GP mortar because of its clay nature. For this purpose and to ensure workability, additives were added to these GP mortars at a rate of 1% of the binder amount. n-ZN was added in increments of %0, %0.25, %0.50, and %0.75. These mixtures containing n-ZN are expressed as ZN 0, ZN 25, ZN 50, and ZN 75 in the study, respectively. Table 3 presents the properties of additive, Table 4 presents the properties of n-ZN, and Table 5 presents the GP mortar mix design in detail.

Table 1. Properties and composition of binder materials

Binder	LOI	MgO	Al_2O_3	Na_2O	K_2O	CaO	Fe_2O_3	SiO_2	Specific gravity
FA	0.91	2.42	22.95	0.92	0.99	2.58	7.25	58.25	2.31 (g/cm^3)
MK	1.11	0.16	40.25	0.24	0.55	0. 91	0.85	56.10	2.52 (g/cm^3)

Table 2. Properties of aggregate

	Grain diameter	Water absorption	Specific gravity
Fine sand	0. 6 mm	2.1	2.72 (g/cm^3)

Table 3. Properties of additive

	Type	Color	Specific gravity
Additive	Viscosity regulator	Green liquid	1.01 (g/cm^3)

Table 4. Properties of n-ZN

Nano-ZnO	
Chemical formula	ZnO
Surface area (m^2/g)	20-65
Color	White
Average particle diameter (nm)	18
Chemical structure	Crystal
Purity (%)	99.99
Shape	Near spherical

Table 5. GP mortar mix design (by mass ratio)

Mix	FA	MK	Nano-ZnO (%)	SM	SH	SS/SH	AAS/B	Aggregate	VRA (%)
ZN 0	0.50	0.50	0.00	0.55	0.25	2.20	0.80	2.57	0.01
ZN 25	0.50	0.50	0.25	0.55	0.25	2.20	0.80	2.57	0.01
ZN 50	0.50	0.50	0.50	0.55	0.25	2.20	0.80	2.57	0.01
ZN 75	0.50	0.50	0.75	0.55	0.25	2.20	0.80	2.57	0.01

***SM:** Na_2SiO_3**, SH:** NaOH**, AAS/B:** alkaline activator solution/binder**, VRA:** viscosity regulator additive

2.2 Mix Design and Method

The GP mortar mixing procedure used in this study follows the steps used in the author's previous study [25]. While printing, the printer speed was set to 80 cm/minute, and a 0.9 x 1 cm rectangular nozzle was employed. The samples were exposed to ambient conditions for 7, 28, 90, and 180 days. Five layers of GP mortar specimens were fabricated by 3D printer, with the layer height of each GP mortar sample designed as approximately 0.8 cm. Figure 1 shows the flow chart of the GP mortar sample produced with a 3D printer.

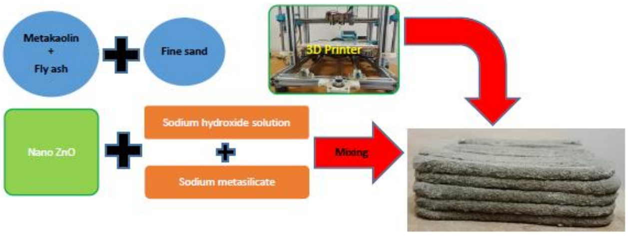

Figure 1. The flow chart of 3DGP mortar

For this study, forty-eight prismatic GP mortar mixture samples of four different types, each measuring 4 cm x 4 cm x 16 cm, were prepared. These samples were then kept under 23±2 °C ambient temperature curing conditions and kept until they reached the specified test ages (7, 28, 90, and 180 days). At the end of the curing periods, the GP mortar samples produced with the 3D printer were subjected to fresh state and hardened property tests.

2.3 Experimental Procedure

2.3.1 Fresh State Testing Procedure

The flowability properties of the produced GP mortars were determined by the flow table test. It was carried out according to ASTM C230 [32]. Fresh GP mortar mixtures were filled into the spreading table in two layers. Each layer was compacted 20 times with a tamper. Then, it was slowly removed and the flow table was lowered 25 times in 15 seconds to ensure spreading on the table. The diameter of the spread fresh GP mortar mass was measured in two perpendicular directions and the measured values were recorded in cm. Then, the flow table was determined by taking the arithmetic average of the values obtained in these two perpendicular directions for each fresh GP mortar sample. The test device used to determine the flowability properties and the GP mortar on which the flow table test was applied are given in Figure 2.

a) **b)**

Figure 2. a) The flow table test device [25], **b)** GP mortar sample

Buildability is the ability to 3D print by adding mortar layer by layer continuously to the required level without significant deformation or collapse of the freshly printed component [33]. The buildability tests, which are of great importance in terms of extrudability and printability properties of 3DGP mortar specimens produced with a 3D printer, were applied. It was carried out according to ASTM C1437 [4]. This test determines the shape retention of fresh GP mortar samples subjected to static load. Each fresh GP mortar mixture was placed in a mini-slump mold shortly after the first mixing. The mold was removed after a waiting period of 60 seconds. To ensure a smooth and equal distribution of the load, a glass plate was placed on the fresh GP mortar sample. Then, a 0.6 kg load was applied with the glass plate weight for 60 seconds. At the end of 60 seconds, the deformation of the fresh GP mortar samples was measured in two perpendicular directions, taking into account the final heights of the samples. The arithmetic averages of these two measured values were taken and the average height values were recorded. At the end of the test, it is accepted that the mixtures with higher final height values can be constructed better. The GP mortar on which the buildability test was applied is given in Figure 3.

Figure 3. The buildability test GP mortar sample.

2.3.2 Hardened State Testing Procedure

UPV and mechanical strength (FS and CS) tests were applied to hardened GP mortar samples produced with a 3D printer. Forty-eight prismatic samples, each measuring 4 cm x 4 cm x 16 cm, for four different GP mortars made up the test for this study. Prismatic specimens measuring 4 x 4 x 16 cm were subjected to FS testing according to ASTM C348 [35] standards using a loading rate of 0.2 kN/s. Three samples were tested for each mixture. At the end of the curing periods, the FS of the GP mortar specimens produced with the 3D printer belonging to each series were obtained by taking the arithmetic average of three samples. Then, the CS of the 3DGP mortar samples were determined in an automatically controlled press according to the ASTM C349 [36] standard. The 3DGP mortar samples, which were cured at ambient temperature and subjected to CS tests at the end of the 7, 28, 90, and 180-day curing periods, were the samples subjected to FS tests and were divided into two for each sample after the test. The arithmetic mean of six specimens was used to determine the CS of the 3DGP mortar specimens that belonged to each series. Figure 4 shows 3DGP mortar samples subjected to FS and CS tests using a mechanical testing device.

a) **b)**

Figure 4. **a**) 3DGP mortar samples subjected to FS, **b)** 3DGP mortar samples subjected to CS

3. Results and Discussion

3.1 Fresh Properties Test Results

3.1.1 Flowability Test Results

The flowability test results of 3DGP mortar samples are given in Figure 5.

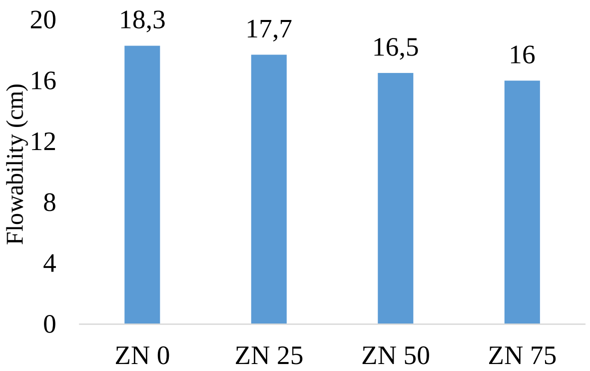

Figure 5. The flowability test results of 3DGP mortar samples

When Figure 5 is examined, the flow tables in the ZN 0, ZN 25, ZN 50, and ZN 75 series were found to be 18.3, 17.7, 16.5, and 16 cm, respectively. n-ZN reinforcement reduces the flowability properties and decreases the flow table values in GP mortars. Nanomaterials have reduced workability due to their large surface area. They also react rapidly with alkaline activators, providing the creation of a viscous, and extremely adhesive GP matrix [28].

3.1.2 Buildability Test Results

Figure 6 displays the outcomes of the 3DGP mortar samples' buildability test.

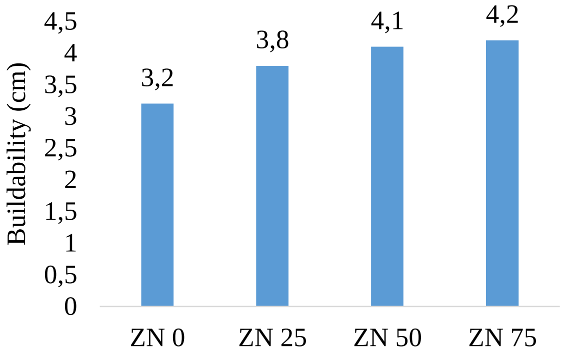

Figure 6. The buildability test results of 3DGP mortar samples

When Figure 6 is examined, the buildability test results of the ZN 0, ZN 25, ZN 50, and ZN 75 series were found to be 3.2, 3.8, 4.1, and 4.2 cm, respectively. Buildability benefits from the quick improvement in yield strength of GP composites that comes from the addition of nanoparticles [33]. In this study, n-ZN was utilized to improve buildability and strength. The literature has investigated the utilization of nanoparticles to boost the yield strength of 3DGP samples. To enhance the buildability of GP composites without considerably compromising their pumpability, it was acceptable to incorporate the nanoparticles during the mixing stage [37]. n-ZN reinforcement increases the buildability properties in 3DGP mortars [25]. This increase was found to be 18.75%, 28.13%, and 31.25% in the series containing n-ZN (ZN 25, ZN 50, and ZN 75) compared to the ZN 0 control series without n-ZN, respectively. As a result, it was discovered that n-ZN use in GP composites was crucial for buildability.

3.2 Hardened Properties Test Results

3.2.1 UPV Test Results

To learn about the strength characteristics of 3DGP mortar specimens, UPV tests were used. The UPV test results of 3DGP mortar samples are given in Figure 7.

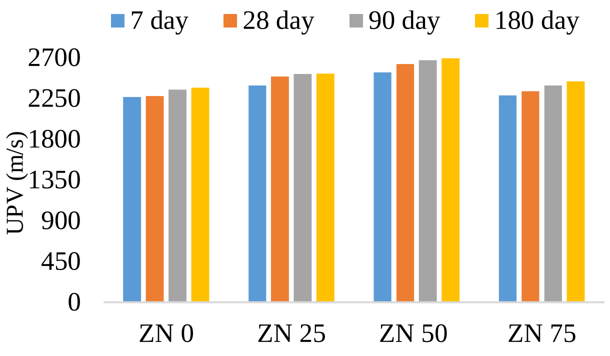

Figure 7. The UPV test results of 3DGP mortar samples

When Figure 7 is examined, the UPV test results of the ZN 0, ZN 25, ZN 50, and ZN 75 series increased in all series in parallel with the increase in cure times. This increase was found to be 10%, 15%, and 2%, respectively, in the series containing n-ZN (ZN 25, ZN 50, and ZN 75) cured at ambient temperature for 28 days, compared to the ZN 0 control series without n-ZN. The highest UPV test values were recorded in the ZN 50 series containing 0.5% n-ZN at the end of all cure times. These results are also consistent with the literature [20]. In the literature, the CS of the specimens improved by 0.5% with the addition of n-ZN, but the CS of the samples reduced with the addition of 0.7% [20]. UPV outcomes are often parallel to CS and are assumed to be related to CS [25]. The UPV test results of the ZN 50 series cured at ambient temperature for 7, 28, 90, and 180 days were found to be 2538 m/s, 2631 m/s, 2674 m/s, and 2695 m/s, respectively.

3.2.2 FS Test Results

The FS test results of 3DGP mortar samples are given in Figure 8.

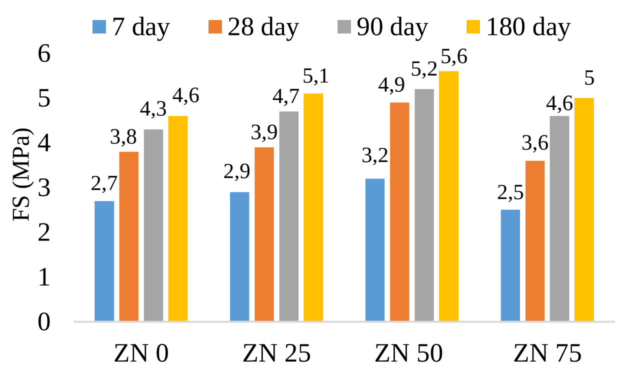

Figure 8. The FS test results of 3DGP mortar samples

When Figure 8 is examined, the FS test results of the ZN 0, ZN 25, ZN 50, and ZN 75 series increased in all series in parallel with the increase in all cure times. This increase was found to be 75%, 63%, and 53%, respectively, in the series containing n-ZN (ZN 25, ZN 50, and ZN 75) cured at ambient temperature for 28 days, compared to the ZN 0 control series without n-ZN. The highest FS test results were obtained in the ZN 50 series containing 0.5% n-ZN at the end of all cure times. Sobhy et al. [38] found that the inclusion of 0.5% n-ZN increased the FS at the end of 28-day curing times by approximately 25%. The worst effect of NZ is that it reduces the mechanical strength and hydration degree when used in composites at a rate higher than 0.5%; all of these are due to the reaction between ZnO and CH. Therefore; the reinforcement of NZ at a rate higher than 0.5% has a bad effect on the mechanical properties of the composite. The literature also has instances of this circumstance. [39, 40].

3.2.3 CS Test Results

The CS test results of 3DGP mortar samples are given in Figure 9.

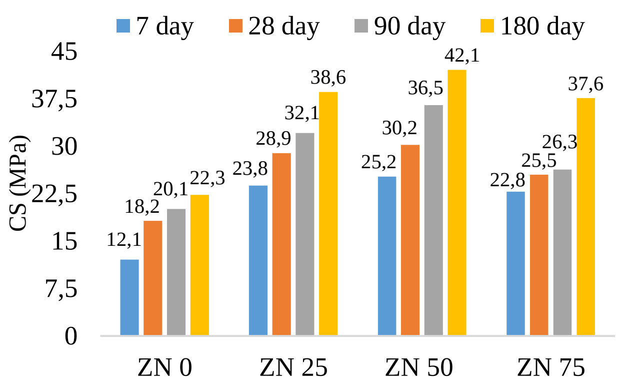

Figure 9. The CS test results of 3DGP mortar samples

When Figure 9 is examined, the CS test results of the ZN 0, ZN 25, ZN 50, and ZN 75 series increased in all series in parallel with the increase in all cure times. This increase was found to be 67.1%, 44.8%, and 19.8%, respectively, in the series containing n-ZN (ZN 25, ZN 50, and ZN 75) cured at ambient temperature for 28 days, compared to the ZN 0 control series without n-ZN. The highest CS test results were obtained in the ZN 50 series containing 0.5% n-ZN at the end of all cure times. n-ZN contributed to the increase in strength by filling the void structures. If homogeneous distribution is provided, no sedimentation and no agglomeration is observed, the type of nanomaterial increases the mechanical performance of the GP mortar depending on the type and rate of addition. The results obtained from this study are supported by the literature [20], [25], [28], [40]. Therefore, the optimum amount of nano zinc oxide to be used in such composites is thought to be 0.5%.

Zidi et al.'s study [20], indicated that when the n-ZN was 0.5%, the CS test was at its highest. They claimed that the decrease in the interfacial transition zone caused by the n-ZN particles' and GPs matrix's interfacial adhesion is the cause of this. Additionally, they stated that at a dosage of 0.7% for n-ZN, the CS dropped as a result of improperly disseminated nanoparticle aggregation [20]. Other research, in addition to this one, has shown that the mechanical properties are decreased when n-ZN is used in amounts more than 0.5% [28], [41]. Zailan et al. [18] found the highest CS test results in 2.5% n-ZN reinforced GP composites cured at ambient temperature for 28 days. In this study, the highest CS was obtained in GP mortars containing 0.5% n-ZN. Raj et al. [28] found that the inclusion of 0.5% n-ZN increased the CS by approximately 26% [23]. Zidi et al. [19], in their paper comparing the cost analyses of different nanomaterials, found that GP samples containing 0.5% n-ZN increased the CS by 26.7%. As in previous research, the maximum CS in this sample came from 3DGP mortar containing 0.5% n-ZN. In this study, approximately 20% CS increase was recorded in 3DGP mortar samples. The CS of the ZN 50 series cured at ambient temperature for 28 days was found to be 30.2 MPa. n-ZN created a filler effect, filled the existing voids, and created a more impermeable structure, causing an increase in the strength of 3DGM samples. This increase is due to the high specific surface area and reactivity of nano-sized materials. As a result of pozzolanic reactions, the increase in strength became more pronounced over time. Therefore, as the curing time increased, the increase in strength continued at 7, 28, 90, and 180 days. In addition, since production is done without using molds, it is more economical and faster, which are other advantageous results in addition to its CS. This strength is sufficient and acceptable for many construction applications.

4. Conclusion

This study investigated the fresh state properties and hardened mechanical strength properties of GP mortars produced with n-ZN reinforcement and cured at ambient temperature conditions. ZN 0 series without nanomaterials were accepted as control samples and the experimental results obtained with n-ZN reinforced 3DGP mortar samples were compared. The obtained results are given below:

1- Buildability test results increased and GP mortar sample flowability values decreased when n-ZN was added to mixtures. The ZN 0 samples produced the greatest flowability and lowest buildability findings. The ZN 75 samples yielded the highest buildability and lowest flowability scores as well. The rheological characteristics of 3DGP mortar samples were found to be improved by the usage of n-ZN in this investigation.

2- The highest UPV results were obtained from the ZN 50 series, with approximately a 15% increase compared to the ZN 0 control samples cured for 28 days. It was determined that UPV results and CS results support each other as in traditional mortar. Therefore, it was concluded that the non-destructive test methods developed to determine the mechanical properties of traditional mortars are valid in 3DGP mortar samples.

3- The greatest FS results were obtained from the ZN 50 series, with approximately a 63% strength increase compared to the ZN 0 control samples cured for 28 days. This increase in FS of GP can be explained by the microstructure developed by the addition of zinc to the GP mortar and the formation of a denser GP mortar as a result of the polymerization reaction.

4- The peak CS of n-ZN reinforced 3DGP mortar samples is obtained using 0.5% nano zinc oxide. This can be attributed to the potential of nanomaterials to fill or minimize voids and the ability of nanozinc to increase the polymerization rate. 3DGP mortar samples containing 0.5% n-ZN gave the highest CS results at all cure times. Approximately 66% higher CS results were obtained from the ZN 50 series than the control samples cured for 28 days.

It has been observed that the fresh state and mechanical properties of 3DGP mortar samples exhibit good performance with a very small amount of n-ZN reinforcement. It is also thought that it would be useful to examine the durability properties of 3DGP mortar samples with n-ZN reinforcement.

Statement of Research and Publication Ethics

The study is complied with research and publication ethics.

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