Effect of Novel Synthesized Nanoeggshell on the Properties of Cementitious Composites

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Abstract

In this study, a novel synthesized form of nanoeggshell is introduced and its use in cementitious composites is proposed as a green, safe and low-cost additive. The nanoeggshell was characterized using FTIR, SEM, BET and viscometer techniques and results showed that the ultrasonic effect was a major factor for the structure of synthesized hierarchical 3D flower-like nanoeggshell. The intrinsic viscosity, voluminosity, and shape factor of nanoeggshell were calculated to understand rheological properties of the structure. Different error functions were used to find the optimum. Regarding the effect of the novel 3D flower-like nanoeggshell on the mechanical properties of mortar, four different cement mortar mixtures were prepared with varying percentages of nanoeggshell (0%, 0.1%, 0.5% and 1%). It is concluded that compressive strength of the mixtures increased with the increasing amount of nanoeggshell additive. Additionally, flexural strain capacity was improved with the additive due to bridging effect in the cement matrix, thus induced higher ductility. In addition, better workability was noted in the mixtures with nanoeggshell. As a result, the introduced 3D flower-like nanoeggshell is a novel potential nanomaterial that can be used as an effective additive for improving the mechanical properties of cementitious composites.

1. Introduction

Cement is the most widely used binder material in concrete mixtures. However, the past decade has seen a renewed importance in minimizing the cement content used in the construction industry because of the huge CO₂ emissions. Apart from the environmental impact, cement-based materials still have major defects such as high brittleness and porosity as well as low ductility and permeability. These factors induce poor resistance to crack formation and low tensile strength and strain capacities.

Steel fibers have been used in order to overcome weakness in ductility and tensile strength of concrete (Akca and Ozyurt 2018; Tiberti et al. 2015; Balendir et al. 2002). Steel fibers serve as barriers to crack since they act as bridges between micro-cracks within the concrete matrix and decrease the crack tip opening displacement. In addition, the incorporation of steel fibers provides an increase in fracture toughness of concrete (Şahin and Köksal 2011). On the other hand, the inclusion of fibers causes a significant reduction in workability (Uygunoğlu 2011). Thus, much greater improvements in mechanical performance can be achieved through altering the microstructural features of concrete beside the strategies that concern modifications of concrete at a macro level.

Recent research topics have focused on improving the concrete performance through the incorporation of nanomaterials in cement to modify the internal matrix of concrete and to overcome the shortcomings of concrete that cause limitations in practice. In light of recent developments in nanotechnology, there is considerable interest in nanomaterials because of their potential of modifying the microstructure and mechanical properties of cement. Because of the improvement of microstructure and densification of cement paste by the addition of nanomaterials, not only the mechanical properties but also the transport properties of cement-based materials improve. Moreover, nanomaterials have the feature of improving the electrical conductivity properties of cementitious composites. Due to these advanced properties, different nanomaterials have been added into cement and many applications have been conducted in the field of construction materials.

The first studies about the effects of the use of nanomaterials in cement-based composites started with zero-dimensional (0D) materials such as nanosilica, nanotitania (Folli et al. 2012), and then reached a significant level with 1D-materials like carbon-nanotubes (Tiong et al. 2018; Kim et al. 2019). The studies have concluded that the addition of nanosilica in cement-based composites leads to the im-
provement of strength and durability and reduction of porosity (Kong et al. 2012, 2013). Some recent studies have drawn attention to the effect of the PVA fibers in the cementitious composites containing nanosilica (Ling et al. 2019; Zhang et al. 2019a, 2019b). The results of these studies have indicated that incorporating nanosilica into cementitious composites enhanced the microscopic structure and increased the tensile strength significantly whereas it had a slight effect on the other studied mechanical properties like compressive strength, flexural strength, and fracture toughness. The effect of particle size on these mechanical properties has been also reported separately (Ling et al. 2020). In another study, by replacing the cement with different percentages of nanosilica and nanoparticles of calcium carbonate, the flowability and durability of PVA fiber reinforced cementitious composites have been examined (Zhang et al. 2019b). It is concluded that both types of nanoparticles have improved durability but also both have decreased flowability. Likewise, the addition of carbon nanotubes in cement-based composites has resulted in an increase in strength and a reduction of porosity (Li et al. 2005; Nochaiya et al. 2011). For the last few years, a carbon-layered, 2-dimensional (2D) graphene material has made significant contributions to the cement matrix in terms of high strength and high specific surface area (Lee et al. 2008; Papageorgiou et al. 2017). Also, graphene oxide, recognized as being graphene derivative, has better dispersion properties compared to graphene (Qureshi and Panesar 2019). Besides, it increases compressive and tensile strength, ductility, and durability of cement-based composites (Lv et al. 2013; Babak et al. 2014; Mohammed et al. 2018; Peng et al. 2019). A recent review on the graphene oxide reinforced cementitious composites detailed the existing studies, underlined the gap in knowledge and also listed the required topics to be studied in near future (Xu et al. 2018). The study has also pointed out that mechanical properties of graphene oxide reinforced cementitious composites have been investigated in most of the studies but that the durability problem has not been sufficiently considered. As a result, the most significant benefits of using these nanomaterials in cementitious materials are stated as highly increased compressive and flexural strength as well as Young’s Modulus; reduction in porosity; the accelerated formation of C-S-H gel structure; and their self-cleaning characteristics (Silvestre et al. 2016). Besides all these benefits, there are still limitations for their practical use due to the high cost in construction applications. Thus, there is a demand for alternative sustainable and cost-efficient nanomaterials to be used in cementitious composites.

Eggshells, natural biological waste, can be considered as one of the potential substitutive materials composed of mainly calcium compounds similar to that of cement and contain about 94% of calcium carbonate, 1% of magnesium carbonate, 1% of calcium phosphate, 4% of organic matter (Mine 2008; Rivera et al. 1999). This pure form of calcium carbonate or limestone, which is also called calcite (CaCO3), can be utilized as a filler or as a partial cement replacement. It is reported that eggshell used in the form of limestone behave similar mechanical properties as commercial lime (Beck et al. 2010).

Eggshell powder is used to decrease the setting time in cement paste since it contains CaO that accelerates the cement hydration (Shiferaw et al. 2019a). The optimum accelerating effect is achieved with 2.5% replacements (Mtallib and Rabiu 2009). There have been also studies about the use of eggshell in the stabilization of road pavements (Okonkwo et al. 2012), production of ceramic wall tiles (Freire and Hollanda 2006) and soil bricks (Siqueira et al. 2016). Moreover, eggshell substituted mortars have been reported as possessing the capability of radioactivity shielding performance (Binici et al. 2015).

Studies reported that derived lime from eggshell powder influences the strength of mortars. Yet controversial results were presented by different researchers. Some studies have reported that compressive and flexural strengths have improved at the eggshell powder substitution level up to 5% by weight of cement but a drastic reduction in strength beyond 5% (Tiong et al. 2018; Gowsika et al. 2014; Yerramala 2014; Ujin et al. 2017; Sivakumar and Mahendra 2014; Rahman et al. 2019). In another study, the eggshell powder is added to the concrete mix as a partial complement to Portland cement and similar compressive strengths were obtained with the control concrete up to 5% additions by weight (Patel et al. 2017). It is also reported that eggshell powder addition reduced the compression and flexural strengths at all levels of Portland cement replacements (Pliya and Cree 2015; Binici et al. 2015; Mazizah et al. 2018; Afizah Asman et al. 2017).

These previous studies have only focused on the powder form of eggshells that have been usually hand-crushed or grinded. The powdered eggshell particles may have an irregular morphology due to the grinding process utilized and may contain quantities of the organic membrane. Moreover, the coarse size of eggshell powder also affects the mechanical properties of the mortars negatively. Therefore, it is expected that nanosized eggshell substitution would form a denser Portland cement paste and as a result, the transition zone between the cement paste and fine aggregates improves the performance of the cementitious composites.

Since eggshells are good candidates for synthesizing high-performance materials in different application areas, synthesized nanof ormulation of eggshells can be of interest due to its properties (economic, safety, thermal and mechanical properties) in construction applications (Khan et al. 2020; Preda et al. 2020). The eggshell in nanoscale was synthesized using different methods such as ball milling (Foroutan et al. 2019), ultrasonic-assisted method (Mosaddegh 2013), thermal decomposition method (Li et al. 2018), and hydrothermal method (Prabakaran and Rajeswari 2009). Khemthong et al.
reported the microwave-assisted eggshell displayed the highest catalytic performance and the microwave method had a role on the chemical reaction due to the electromagnetic radiation in a short time. Vichaphund et al. (2011) showed that the microwave-assisted eggshell could be used to synthesize uniform shaped wollastonite. Mosaddegh (2013) showed that the ultrasonically assisted method could be used to synthesize the nanoeggshell powder based on acoustic cavitation. Despite this interest, to the best of our knowledge, in the literature, there seem to be no studies using the dual effect of ultrasonic and microwave method in preparing nanoeggshell. De-sonically assisted method could be used to synthesize the nanoeggshell. Based on the information in the literature, the microwave-ultrasound-assisted method is used for the first time to prepare nanoeggshell in this study.

With this motivation, the objectives of this study are (1) to prepare a novel hierarchical 3D flower-like nanoeggshell with a green chemistry approach, (2) to investigate the rheological property of nanoeggshell, and (3) to evaluate mechanical properties of cementitious composites containing nanoeggshell. This paper is a preliminary attempt to use the solution form of the white eggshell could be used to synthesize uniform shaped nanoeggshell. Consequently, proposes the novel nanoeggshell as a green, safe and low-cost additive in construction applications.

2. Materials and methods

2.1 Materials

Ordinary Portland cement (PC 42.5 R) acquired from Akçansa cement factory was used as the binder in this study. River sand (0 - 5 mm) was used as fine aggregate. The white eggshells that were used as nanosized additive in mortar were obtained from a local region (Pendik) of Istanbul, Turkey. Deionized water (18 MΩ) was prepared in an ultra-purification system (Millipore, USA). Glacial acetic acid (99 - 100%) and ethanol were purchased from Merck Company. All reagents were of analytical grade and used as received without further purification.

2.2 Preparation of eggshell

The eggshell was washed with deionized water three times. The inner membrane of the eggshell was removed. The eggshell was put in the microwave oven and treated for 5 minutes at 720 W. Then, the eggshell was washed with deionized water three times again and treated for 5 minutes at 720 W. The dried eggshell was ground in the mortar and was sieved to 74 microns. The powder of eggshell was treated with a mixture of 25 ml water/25 ml ethanol solution in a ratio of 1:1 v/v, filtered and dried for 5 minutes at 720 W. 0.1 grams of powder eggshell was added to 1 ml glacial acetic acid/49 ml water solution and sonicated for 1 h. Finally, the solution was filtered by a 0.22-micron membrane and stored in a sterile container at room temperature for use.

2.3 Characterization of eggshell

Scanning Electron Microscopy (JEOL 63335F model), FTIR (Perkin Elmer Spectrum Two FT-IR Spectrometer), (4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹ using 8 scans and KBr powder), and viscometer (AND model) were used to determine the morphological properties of the nanoeggshell. The specific surface area of nanoeggshell was determined using Brunauer-Emmett-Teller (BET) method (Micromeritics Gemini 2360 model).

2.4 Rheological properties of nanoeggshell

The intrinsic viscosity ([η]), the voluminosity (Vη), and the shape factor (ν) of nanoeggshell were calculated to understand the rheological properties of structure [Eqs. (1) to (4)]. In the measurements, the viscosity was measured three times using an AND viscometer (25 ± 0.5°C, 50 ml sample). The [η] was calculated using the values of the relative viscosity ([η]rel) and the specific viscosity ([η]sp) (Karakuş 2019; Karakuş et al. 2019; Tonelli and Masuelli 2019; Cherif 2019; Liu et al. 2019; Joseph et al. 1991; Boulet et al. 1998; Antoniou et al. 2010).

\[ [\eta] = \frac{\eta_{\text{rel}}}{C} = \frac{n_{\text{rel}} - 1}{C} = \frac{t - 1}{C} \] (1)

where \( t_0 \) is the flow time of the pure solvent and \( t \) is the flow time of the solution.

The Huggins regression model was used to explain the viscosity characteristics of the solution and calculate the Huggins parameters \([\eta] \) and \( k \).

\[ [\eta] = \frac{\eta_{\text{rel}}}{C} = \frac{n_{\text{rel}} - 1}{C} \] (2)

\[ [\eta] = \nu V_{\eta} \] (3)

\[ \gamma = \frac{\eta_{\text{sp}}^2 - 1}{C(1.35\eta_{\text{sp}}^2 - 0.1)} \] (4)

Different error functions were used as Marquardt's percent standard deviation (MPSD), hybrid fractional error function (HYBRID), and the average relative error (ARE) were calculated to find the optimum \([\eta] \) using Eqs. (5), (6) and (7), respectively (AkankshaKalra et al. 2019; Kar et al. 2019; Mallakpour and Tabesh 2019).

\[ \text{MPSD} = 100\sqrt{\frac{1}{(n-p)}\sum_{i=1}^{n-p} \left( \frac{q_{i,\text{meas}} - q_{i,\text{cal}}}{q_{i,\text{meas}}} \right)^2} \] (5)

\[ \text{HYBRID} = 100\sqrt{\frac{1}{(n-p)}\sum_{i=1}^{n-p} \left( \frac{q_{i,\text{meas}} - q_{i,\text{cal}}}{q_{i,\text{meas}}} \right)^2 \left( \frac{q_{i,\text{meas}}}{q_{i,\text{cal}}} \right)} \] (6)

\[ \text{ARE} = 100\sqrt{\frac{1}{(n-p)}\sum_{i=1}^{n-p} \left( \frac{q_{i,\text{meas}} - q_{i,\text{cal}}}{q_{i,\text{meas}}} \right)^2} \] (7)

where \( n \) is the number of data points, \( p \) is the number of parameters and \( q_{i,\text{meas}} \cdot q_{i,\text{cal}} \) are the measured and calculated capacities, respectively.

2.5 Mortar specimen preparation

Prismatic mortar specimens with dimensions of 40 × 40 × 160 mm were cast in steel molds. A standard cement :
sand : water (2 : 2 : 1) ratio was used for all mortar mixtures where adequate workability was monitored. No superplasticizer was used. Nanoeggshell additives were incorporated in four different ratios, 0%, 0.1%, 0.5% and 1% by weight with respect to binder content. Throughout this paper, the acronym NES denotes for nanoeggshell and the mixtures with 0.1%, 0.5% and 1% nanoeggshell content are named as NES1, NES5 and NES10, respectively. All mixture compositions are given in Table 1. Since additives were in liquid form, water content was configured with the increasing additive amount to sustain the liquid to binder ratio for all mixtures.

All mixtures were mixed with a Hobart mixer. Cement and river sand were dry mixed for 1 minute and subsequently, the eggshell additive was included and mixing was continued for 2 minutes. All specimens were demolded after 24 h and were stored in water tanks at a curing temperature of 20°C.

2.6 Flowability of mortar specimens

The flowability of mortar mixtures was tested according to ASTM C1437-15 (ASTM 2013) which is the standard method for the flow of hydraulic cement mortar. The test was carried out with a jumping table with a flow mold filled with mortar mixture to its full height of 50 mm in two layers by tamping 20 times for both layers. After the mold was lifted, the jumping table was dropped for 25 times in 15 seconds. The diameter of the mortar along two vertical directions were measured and assessed as bigger diameters showing better workability.

2.7 Mechanical tests

Flexural and compressive strength tests were conducted on all mixtures. For every specimen type, six specimens were cracked under flexural loads and two portions formed were crushed under compressive loading, thus making a total of 12 specimens for compression strength testing. Flexural loading was done with an MTS closed-loop servo-hydraulic test system under a three-point loading test fixture. Displacement controlled flexural loading was performed with a loading rate of 0.5 mm/min for all specimens. A linear variable differential transformer was placed vertically under the midspan of the prismatic specimens prior to testing and vertical displacement data obtained were used to moderate the loading rate in a closed-loop system. Displacement controlled loading ramp was selected to monitor any change in strain capability subsequent to including the additive in different percentages. Compressive strengths of samples were determined according to TS EN 196-1 (TSI 2016) standard. Half prisms formed after flexural strength tests were used in compressive strength testing. Force controlled compressive loading was applied at a speed of 0.6 MPa/sec.

3. Results and discussion

3.1 Characterization of nanoeggshell

The morphology of hierarchical 3D flower-like nanoeggshell was investigated by SEM technique. The SEM images of hierarchical 3D flower-like nanoeggshell are given in Fig. 1 with different magnifications. It was observed from the SEM images that the nanostructure did not show aggregation and the nanoeggshells had 3D flower-shaped morphology with lengths below 100 nm of capillary arms. As similar results, Foroutan et al. (2019) reported that the eggshell nanoparticles were spherical with a non-uniform size. Mosaddegh (2013) found that the nanoeggshell powder had a large surface area and the average size of the nanostructure was 50 nm. The FTIR spectrum of hierarchical 3D flower-like nanoeggshell is shown in Fig. 2. The results showed that hierarchical 3D flower-like nanoeggshell consisted of calcium carbonate. In Fig. 2, peaks were observed at 3502 cm⁻¹ (-OH), 2985 cm⁻¹ (-CH), 2870 cm⁻¹ (C=O), and 1610 cm⁻¹ (C=C). Also, characteristic peaks occurred at 1545 cm⁻¹, 1480 cm⁻¹, 890 cm⁻¹ and 710 cm⁻¹.
due to CaCO₃ (Foroutan et al. 2019; Syafiq et al. 2020). Lu et al. (2016) found similar FTIR results.

The surface area of nanoeggshell was measured using BET. According to BET analysis, the surface area of nanoeggshell was found 220.2 m²/g. In the study of the conversion of waste eggshells to mesoporous hydroxyapatite nanoparticles was found high surface area (212.4 m²/g). Therefore, our result also confirms the previous findings in the literature (Ibrahim et al. 2020).

3.2 Viscosity studies
Examining the rheological properties of colloidal systems is very important in explaining the properties of nanostructures. It is known that the efficiency of new materials improves when homogeneously dispersed particles are produced. As the stability of the colloidal systems is significant and complex, a high fluidity property is vital (Jachimska and Adamczyk 2007). Rheological properties play a role in determining some factors such as the size, the shape, the size distribution, the formation of aggregates and their network structure in producing a stable nanostructure (Di Giuseppe et al. 2012; van der Werff and de Kruijff 1989; Çiftçi et al. 2008). Viscosity analyses have been used to characterize the rheological properties of macromolecular dispersions (Rao 2020; Karakuş et al. 2020; Karakuş 2019). The rheological properties of nanoeggshell played a very important role for the stability of structure. For this purpose, in order to obtain a stable structure in different experimental conditions, sonication time and salt effect were examined and rheological properties were illuminated.

The rheological properties of the eggshell solutions were examined using a viscometer (AND model, Japan) in a thermostatic bath under precise temperature control (± 0.1°C) in 10 ml of sample at 1 min. In order to determine the viscosity behaviors of the sample, rheological parameters such as [η], volumetric (Vₑ) and shape factor (υ) of the nanoeggshell were calculated. The intrinsic viscosity of the sample was calculated using the Huggins model with a high correlation constant (R²). The change in [η] at different sonication times is given in Fig. 3. The intrinsic viscosities of the samples synthesized at different sonication times (10 min, 30 min and 1 h) were calculated using the Huggins model with a high correlation constant (R²) and these values were 0.9979 for 10 min, 0.9972 for 30 min, and 0.9999 for 1 h, respectively. As can be seen in Fig. 3, the value of [η] decreased with increased sonication time.

The intrinsic viscosity for the nanoeggshell was calculated by employing Huggins model at different sonication times. It was found that the nanoeggshell with the sonication time of 1 h had the lowest [η] at room temperature. Mahbubul et al. (2014) reported that the sonication had a role on colloidal structure and viscosity of nanostructure. Achieving similar results with our study, Asadi et al. (2019) found that increasing the sonication time was related to decreasing the viscosity of nanostructure.

The values of shape factor (υ) for nanoeggshell indicate a spherical shape-like structure and it was clear that the voluminosity (Vₑ) of sample decreased as the sonication time increased (Table 2).

Table 2 Voluminosity and shape factors for nanoeggshell.

| Time  | Vₑ (dL/g) | υ         | Shape    |
|-------|----------|-----------|----------|
| 10 min| 3.15     | less than 2.5 | Spherical|
| 30 min| 0.88     | less than 2.5 | Spherical|
| 1 h   | 0.73     | less than 2.5 | Spherical|

*Values are mean values ± standard deviation (SD) for triplicate determination

Under optimal conditions of the system, different error functions (Marquardt's percentage standard deviation (MPSD), hybrid fractional error function (HYBRID) and mean relative error (ARE)) were used to find the value of [η]. Table 3 proves that the MPSD method was found to be the most appropriate method for calculating [η] where the experimental and theoretical value known was closest.
The change of $[\eta]$ at different concentrations of NaOH is given in Fig. 4 and it was found that the nanoeggshell had the lowest $[\eta]$ value at room temperature in 0.1 M NaOH. We proved that the viscosity decreased with the addition of NaOH. Amani et al. (2016) found that salt had a profound effect on rheological properties.

The specific gravity of nanoeggshell was determined by diluting a stock saturated salt solution with distilled water. The specific gravity of the nanoeggshell was measured as 1.20 at 4°C. These values also correlate favorably with the results presented by Jóźwiak et al. (2020).

### 3.3 The flow of mortar mixture

Flow diameters of four different mixtures were measured according to specifications in ASTM C1437-15 (ASTM 2013) and flow percentages were obtained and are presented in Table 4. Higher workability was monitored for NES5 and NES10 mixtures with 0.5% and 1% nanoeggshell additive, respectively, whereas not much difference was observed for NES1 mixtures with 0.1% additive. Filler effect of nanoparticles arising from their very low diameter size most probably influenced agglomeration and supplied better dispersion between cement particles and water thus upgrading the hydration process.

### 3.4 Mechanical test results of mortar specimens

The 7 and 28-day compressive strength test results are given in Fig. 5. No significant differences were noticed when 7-day the compressive strengths were compared for all additive ratios. However, when the 28-day compressive strength test results were analyzed, it could be seen that there was a significant amount of increase in the specimens with additive inclusion. Also, it was observed that with the increasing additive content, the effect of additive inclusion was more pronounced. NES1 specimens, which incorporate 1 per mille of eggshell additive with respect to cement weight, did not show much difference in the compressive strength results at both 7 days and 28 days. However, NES5 specimens exhibited a 7% increase whereas NES10 specimens exhibited a 9% increase in compressive strength. It can be concluded that the enhanced workability of the specimens with 0.5% and 1% nanoeggshell additive has contributed to better

![Fig. 3 Huggins models of nanoeggshell with different sonication time.](image)
dispersion and denser cement matrix leading to the higher compressive strengths attained by NES5 and NES10. Incorporation of nanomaterials in cement composites has been reported to affect the hydration process of cement matrix through the formation of nucleation sites thus accelerating the degree of hydration (Shirefaw et al. 2019b). However, the results obtained from the compression tests revealed that, although the reactions may have been accelerated, the inclusion of the new nanomaterial has slightly affected the early strength of specimens comparing with the control specimens. Therefore, it might be attributed as a pozzolanic effect of nanoeggshell additive on interfacial transition zone creating a more compact structure.

Flexural strength results for 7 and 28 days are depicted in Fig. 6. Differences between flexural strengths were not found to be as significant as compressive strength results. 7-day results were not adequate to come to any conclusion about additive inclusion, likewise 28-day results flexural strength results were not enhanced to a significant level. However, minor increments with increasing additive level were detected.

When the 7-day and 28-day results were compared for compressive strength it was seen that early compressive strengths were not affected by additive inclusion while this effect was apparent on 28-day results. For flexural strength analysis, early strength results did not seem to be promising. However, specimens with increasing additive content were found to be higher than control specimens in the 28-day results. For NES10 specimens, an increase of flexural strength was found to be only 3%, which may not be considered as a significant amount to be mentioned.

In Fig. 7, flexural strength versus strain value curves
for four different specimens with four different additive amount are given. Especially specimens that are close to average flexural strength results are given for better assessment of strain behavior of specimens.

Effect of additive inclusion was found to be promising when strain values were examined. It was seen that a highly significant amount of increase in strain capacity of specimens with increasing additive amount was observed which was highly promising since a major deficiency of standard concrete is known to be low ductility, especially under flexural stresses.

As listed in Table 5, control specimens attributed maximum strain values with an average of 3.41‰ and between all mixes control specimens showed minimum strain values. It has to be noted that specimens experienced higher strain values with increasing additive ratios whereas specimens with 0.5% and 1% ratios experienced close values to each other for both flexural strength and strain. The averages of maximum strain values for mixtures with additive inclusion were found to be 4.02, 5.41 and 5.75‰ for NES1, NES5 and NES10 specimens, respectively. These results showed that additive inclusion has attributed much to strain capability of mortar specimens. Similar to other nanomaterials, incorporation of nanoeggshells has probably induced the delayed initiation of microcracks in the cement matrix leading to improved strain capacity, thus deforming ability before crushing was developed (Gong et al. 2015). Moreover, implementation of flower like nanoparticles influenced the interaction in the mortar composites, hence creating better anchorage (Chuah et al. 2014). As has been reported in the literature, the inclusion of GO in cement

| Mixtures | ε_{av} (%) |
|----------|------------|
| Control  | 3.41       |
| NES1     | 4.02       |
| NES5     | 5.41       |
| NES10    | 5.75       |

Fig. 6 7-day and 28-day flexural strength results of specimens with different additive ratios.

Fig. 7 Flexural strength versus strain curves.
composites might probably avoid crack propagation within the cement matrix at nanoscale (Makar 2011). Hence, in this study, the improvements in strain capacity can be attributed to the crack-arresting effects due to the addition of nanomaterial in the mixture.

### 3.5 Microstructural observations of mortar specimens

Workability of the mixtures with higher additive amount contributed to better hydration in inner structure of cement matrix. Thus, it should be easily said that better formation of hydration products was formed. Especially uniform formation of CSH phase must have been conclusive creating a good bonding within the mortar specimens. In literature, it is generally approved that higher surface area for ordinary cement reflects higher degree of hydration and accordingly with the ultra-high specific surface area of nanoeggshell used in cement mortar, thus hydration process is most probably promoted creating higher amount of CSH and better dispersion of hydration products (Pan et al. 2015). Larger specific surface area was also attributed to strong bonding between interfacial transition zone and the cement matrix (Gong et al. 2015).

In Fig. 8, scanning electron microscopy (SEM) visuals of three different mixtures at 28 days and at a magnification of 4000 are given for specimens incorporating 0%, 0.5% and 1% nanoeggshell additive. For NES10 specimen, generally higher amount of hydration products was observed whereas for control specimen, the amount of unhydrated cement particles was more evident. Concluding by the overall visual observations of SEM analysis, the amount of unhydrated cement particles can be sorted as Control > NES5 > NES10.

In previous studies on several nanomaterials, it is known that nanoparticles such as graphene oxide form strong interfacial bonding with the cement matrix if well dispersed (Lu et al. 2016; Chuah et al. 2014). Nanoeggshell exhibited good dispersion ability and very low aggregation when investigated in SEM observations as explained in Section 3.1. High amount of capillary arms with 100 nm length should have been helpful increasing the adhesion between the cement matrix and the sand particles. Consequently, it should be said that 3D flower shaped morphology bear important potential to enhance overall properties of cementitious composites.

### 4. Conclusions

In this study, a novel hierarchical 3D flower-like nanoeeggshell was prepared using the microwaved-ultrasound-assisted method. The rheological properties and mechanical properties of nanoeeggshell on cement mortar were investigated. First, the rheological properties of nanoeeggshell with different concentrations of NaOH and sonication time were studied. When the Huggins model was applied with a high correlation constant, the most appropriate error model was found as MPSD. From the FTIR results, the characteristic peak of CaCO3 was observed in nanoeeggshell. According to the SEM images, the nanoeeggshell had a 3D flower-shaped morphology with lengths below 100 nm of capillary arms. The surface area of nanoeeggshell was 220.2 m²/g and its specific gravity was 1.20.

In order to understand the effect of the solution form of 3D flower-shaped nanoeeggshell in cement mortar mixture, four different cement mortar mixtures were prepared by adding the nanoeeggshell with varying ratios of 0%, 0.1%, 0.5% and 1% by weight of cement. As the fresh state properties were determined, better workability was observed and correspondingly a denser matrix was formed, especially for the mixtures possessing 0.5% and 1% additive content. As evidenced by the compression test results, the compressive strengths of the mortar mixtures were significantly increased with the increasing amount of eggshell additive inclusion, depending on the fact that the workability of the specimens was enhanced and better dispersion in the composite was satisfied. Particularly, the inclusion of the additives in the cement mixtures by 0.5% and 1% content has led to a 7% and 9% increase in 28-day compressive strength results, respectively. Despite the fact that flexural strengths of the specimens were slightly improved by the increasing amounts of additive inclusion, the maximum strain results indicate clearly that flexural strain capacity was considerably enhanced by the increasing contents of additive inclusion. Thus, in this study, it is outlined that remarkable improvements in the ductility of the cement mortars could be achieved through the inclusion of the proposed nanomaterial in cement mixtures.

In conclusion, within this study, considerable progress has been made with regard to the use of nanoeeggshell in cementitious composites. The results of this study sup-

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**Fig. 8 SEM images of mortar specimens at a magnification of 4000:** (a) Control, (b) NES5 and (c) NES10.
port that the novel nanoeggshell is a potential nanostructure candidate for construction applications. Hence, in this study, the novel solution form of nanoeggshell is introduced and its use in cementitious composites as nanomaterial is proposed to be eco-friendly and cost-efficient alternative.

References

Afizah Asman, N. S., Dullah, S., Lynn Ayog, J., Amaludin, A., Amaludin, H., Lim, C. H. and Baharum, A., (2017). “Mechanical properties of concrete using eggshell ash and rice husk ash as partial replacement of cement.” MATEC Web of Conferences, 103-01002.

Akanksha Kalra, H. P., Hui, C. W., Mackey, H., Ansari, T. A., Saleem, J. and McKay, G., (2019). “Adsorption of dyes from water on to bamboo-based activated carbon-error analysis method for accurate isotherm parameter determination.” Journal of Water Science and Engineering, 1(1), 1-11.

Akca, A. H. and Özyurt, N., (2018). “Deterioration and recovery of FRC after high temperature exposure.” Cement and Concrete Composites, 93, 260-273.

Amani, M., Khorasani, M. H. M. and Ghamary, M. H., (2016). “Effect of salinity on the viscosity of water based drilling fluids at elevated pressures and temperatures.” In: Proceedings of the Qatar Annual Research Conference, Doha 22-23 March 2016. Doha, Qatar: Qatar Foundation for Education, Science and Community Development, Article ID EEEP2318.

Antoniou, E., Themistou, E., Sarkar, B., Tsianou, M. and Alexandridis, P., (2010). “Structure and dynamics of dextran in binary mixtures of a good and a bad solvent.” Colloid and Polymer Science, 288(12-13), 1301-1312.

Asadi, A., Pourfattah, F., Mikklos Szilagyi, I., Afrand, M., Zyla, G., Seon Ahn, H., Wongwises, S., Minh Nguyen, H., Arabkoohsar, A. and Mahian, O., (2019). “Effect of sonication characteristics on stability, thermophysical properties, and heat transfer of nanofluids: a comprehensive review.” Ultrasonics Sonochemistry, 58, 104701.

ASTM, (2013). “ASTM C1437 - Standard test method for flow of hydraulic cement mortar.” West Conshohocken, Pennsylvania, USA: ASTM International.

Babak, F., Abolfazl, H., Alimorad, R. and Parvizi, G., (2014). “Preparation and mechanical properties of graphene oxide: cement nanocomposites.” The Scientific World Journal, Article ID 276323.

Balrendran, R., Zhou, F., Nadeem, A. and Leung, A. Y., (2002). “Influence of steel fibres on strength and ductility of normal and lightweight high strength concrete.” Building and Environment, 37(12), 1361-1367.

Beck, K., Brunetaud, X., Mertz, J. D. and Al-Mukhtar, M., (2010). “On the use of eggshell lime and tuffeau powder to formulate an appropriate mortar for restoration purposes.” Geological Society Special Publication, 331, 137-145.

Binici, H., Aksogan, O., Sevinc, A. H. and Cinpolat, E., (2015). “Mechanical and radioactivity shielding performances of mortars made with cement, sand and egg shells.” Construction and Building Materials, 93, 1145-1150.

Boulet, M., Britten, M. and Lamarche, F., (1998). “Voluminosity of some food proteins in aqueous dispersions at various pH and ionic strengths.” Food Hydrocolloids, 12(4), 433-441.

Cherif, E., (2019). “A new correlation of viscosity and conductivity for the polyelectrolyte solutions of poly (sodium styrene sulphonate) (PSSNa) in N,N-dimethylformamide + water.” Physics and Chemistry of Liquids, 1, 10.

Chuah, S., Pan, Z., Sanjayan, J. G., Wang, C. M. and Duan, W. H., (2014). “Nano reinforced cement and concrete composites and new perspective from graphene oxide.” Construction and Building Materials, 73, 113-124.

Çifçi, D., Kahyaoglu, T., Kapucu, S. and Kaya, S., (2008). “Colloidal stability and rheological properties of sesame paste.” Journal of Food Engineering, 87(3), 428-435.

Dr Giuseppe, E., Davaille, A., Mittelstaedt, E. and François, M., (2012). “Rheological and mechanical properties of silica colloids: from Newtonian liquid to brittle behaviour.” Rheologica Acta, 51(5), 451-465.

Folli, A., Pochard, I., Nonat, A., Jakobsen, U. H., Shepherd, A. M. and Macphee, D. E., (2010). “Engineering photocatalytic cements: understanding TiO2 surface chemistry to control and modulate photocatalytic performances.” Journal of the American Ceramic Society, 93(10), 3360-3369.

Foroutan, R., Mohammadi, R., Farjadfard, S., Esmaeili, H., Ramavandi, B. and Sorial, G. A., (2019). “Eggshell nano-particle potential for methyl violet and mercury ion removal: surface study and field application.” Advanced Powder Technology, 30(10), 2188-2199.

Freire, M. N. and Holanda, J. N. F., (2006). “Characterization of avian eggshell waste aiming its use in a ceramic wall tile paste.” Cerâmica, 52(324), 240-244.

Gong, K., Pan, Z., Korayem, A. H., Qi, L., Li, D., Collins, F., Wang, C. M. and Duan, W. H., (2015). “Reinforcing effects of graphene oxide on portland cement paste.” Journal of Materials in Civil Engineering, 27(2), 1-6.

Gowsika, D., Kokila, S. S. and Sargunan, K., (2014). “Experimental investigation of egg shell powder as partial replacement with cement in concrete.” International Journal of Engineering Trends and Technology, 14(1), 65-68.

Ibrahim, A. R., Wei, W., Zhang, D., Wang, H. and Li, J., (2013). “Conversion of waste eggshells to mesoporous hydroxyapatite nanoparticles with high surface area.” Materials Letters, 110, 195-197.

Jachimska, B. and Adamczyk, Z., (2007). “Characterization of rheological properties of colloidal zirconia.” Journal of the European Ceramic Society, 27(5), 2209-2215.
Joseph, R., Devi, S. and Rakshit, A. K., (1991). “Viscosity behaviour of acrylonitrile acrylate co-polymer solutions in dimethyl formamide.” Polymer International, 26(2), 89-92.

Józwiak, B. and Boncel, S., (2020). “Rheology of ionanofluids - a review.” Journal of Molecular Liquids, 302, 112568.

Kar, M. K. A., Fazaeli, R., Manteghi, F. and Ghahari, M., (2019). “Structural, optical, and isothermic studies of CuFe2O4 and Zn-doped CuFe2O4 nanoferrite as a magnetic catalyst for photocatalytic degradation of direct red 264 under visible light irradiation.” Environmental Progress and Sustainable Energy, 38(4), 13109.

Karakuş, S., (2019). “Preparation and rheological characterization of Chitosan-Gelatine@ZnO-Si nanoparticles.” International Journal of Biological Macromolecules, 137, 821-828.

Karakuş, S., Ilgar, M., Kahyaoglu, I. M. and Kilislioglu, A., (2019). “Influence of ultrasound irradiation on the intrinsic viscosity of guar gum-PEG/rosin glycerol ester nanoparticles.” International Journal of Biological Macromolecules, 141, 1118-1127.

Karakuş, S., Ilgar, M., Tan, E., Muge Sahin, Y., Tasaltin, N. and Kilislioglu, A., (2020). “The viscosity behaviour of PEGylatedboparticles.” In: S. Karakuş, Ed. Colloid Science in Pharmaceutical Nanotechnology. London: Intech Open.

Khan, S. R., Jamil, S., Ali, S., Khan, S. A., Mustaqueem, M. and Janjua, M. R. S. A., (2020). “Synthesis and structure of calcium-tin hybrid microparticles from egg shell and investigation of their thermal behavior and catalytic application.” Chemical Physics, 530, 110613.

Khemthong, P., Luadthong, C., Nualpaeng, W., Changsuan, P., Tongprem, P., Viriya-Empikul, N. and Faungnawakij, K., (2012). “Industrial eggshell wastes as the heterogeneous catalysts for microwave-assisted biodiesel production.” Catalysis Today, 190(1), 112-116.

Kim, G. M., Nam, I. W., Yang, B., Yoon, H. N., Lee, H. K. and Park, S., (2019). “Carbon nanotube (CNT) incorporated cementitious composites for functional construction materials: the state of the art.” Composite Structures, 227, 111244.

Kong, D., Du, X., Wei, S., Zhang, H., Yang, Y. and Shah, S. P., (2012). “Influence of nano-silica agglomeration on microstructure and properties of the hardened cement-based materials.” Construction and Building Materials, 37, 707-715.

Kong, D., Su, Y., Du, X., Yang, Y., Wei, S. and Shah, S. P., (2013). “Influence of nano-silica agglomeration on fresh properties of cement pastes.” Construction and Building Materials, 43, 557-562.

Lee, C., Wei, X., Kysar, J. W. and Hone, J., (2008). “Measurement of the elastic properties and intrinsic strength of monolayer graphene.” Science, 321(5887), 385-388.

Lee, H. S., Balasubramanian, B., Gopalakrishna, G. V. T., Kwon, S. J., Karthick, S. P. and Saraswathy, V., (2018). “Durability performance of CNT and nanosilica admixed cement mortar.” Construction and Building Materials, 159, 463-472.

Li, G Y, Wang, P M. and Zhao, X., (2005). “Behavioral mechanism and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes.” Carbon, 43(6), 1239-1245.

Li, Y., Hui, B., Gao, L., Li, F. and Li, J., (2018). “Facile one-pot synthesis of wood based bismuth molybdate nano-eggshells with efficient visible-light photocatalytic activity.” Colloids and Surfaces A: Physicochemical and Engineering Aspects, 556, 284-290.

Li, Z., Wang, H., He, S., Lu, Y. and Wang, M., (2006). “Investigations on the preparation and mechanical properties of the nano-alumina reinforced cement composite.” Materials Letters, 60(3), 356-359.

Ling, Y. F., Zhang, P., Wang, J. and Shi, Y., (2020). “Effect of sand size on mechanical performance of cement-based composite containing PVA fibers and nano-SiO2.” Materials, 13(2), 325.

Ling, Y., Zhang, P., Wang, J. and Chen, Y., (2019). “Effect of PVA fiber on mechanical properties of cementitious composite with and without nano-SiO2.” Construction and Building Materials, 229, 117068.

Liu, X., Lin, W., Astruc, D. and Gu, H., (2019). “Syntheses and applications of dendronized polymers.” Progress in Polymer Science, 96, 43-105.

Lu, S., Yuan, Z., Liu, J., Lu, L. and Hao, H., (2016). “Binding effects and mechanisms of the carboxymethyl starch modified with nano-CaCO3 in magnetite concentrate pellets.” Powder Technology, 301, 1183-1192.

Lv, S., Ma, Y., Qiu, C., Sun, T., Liu, J. and Zhou, Q., (2013). “Effect of graphene oxide nanosheets of microstructure and mechanical properties of cement composites.” Construction and Building Materials, 49, 121-127.

Mtllib, M. O. A. and Rabiu, A., (2009). “Effects of eggshells ash (ESA) on the setting time of cement.” Nigerian Journal of Technology, 28(2), 29-38.

Mubahul, I. M., Chong, T. H., Khaleduzzaman, S. S., Shahrl, I. M., Saidur, R., Long, B. D. and Amalina, M. A., (2014). “Effect of ultrasonication duration on colloidal structure and viscosity of alumina-water nanofluid.” Industrial and Engineering Chemistry Research, 53(16), 6677-6684.

Makar, J., (2011). “The effect of SWCNT and other nanomaterials on cement hydration and reinforcement.” In: K. Gopalkrishnan, B. Birgisson P. Taylor and N. O. Attoh-Okin Eds. Nanotechnology in Civil Infrastructure. Berin and Heidelberg: Springer, 103-130.

Mallakpour, S. and Tabesh, F., (2019). “Tragacanth gum based hydrogel nanocomposites for the adsorption of methylene blue: comparison of linear and non-linear forms of different adsorption isotherm and kinetics models.” International Journal of Biological Macromolecules, 133, 754-766.
Mazizah, E. M., Ali, A. M., Alicia, Y. Y. M. and Nur, N. A. R., (2018). “Characterization of palm oil fuel ash and eggshell powder as partial cement replacement in concrete.” IOP Conference Series: Materials Science and Engineering, 431(3), 1-9.

Mine, Y., (2008). “Egg bioscience and biotechnology.” New York: Wiley & Sons.

Mohammed, A., Al-Saadi, N. T. K. and Sanjayan, J., (2018). “Inclusion of graphene oxide in cementitious composites: state-of-the-art review.” Australian Journal of Civil Engineering, 16(2), 81-95.

Mosaddegh, E., (2013). “Ultrasonic-assisted preparation of nano eggshell powder: a novel catalyst in green and high efficient synthesis of 2-aminochromenes.” Ultrasons Sonochemistry, 20(6), 1436-1441.

Nochaiya, T. and Chaipanich, A., (2011). “Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials.” Applied Surface Science, 257(6), 1941-1945.

Okonkwo, U. N., Odiong, I. C. and Akpabio, E. E., (2012). “The effects of pyrite ash on the compressive strength properties of briquettes.” KSCE Journal of Civil Engineering, 16(7), 1225-1229.

Pan, Z., He, L., Qiu, L., Korayem, A. H., Li, G., Zhu, J. W., Collins, F., Li, D., Duan, W. H. and Wang, M. C., (2015). “Mechanical properties and microstructure of a graphene oxide-cement composite.” Cement and Concrete Composites, 58, 140-147.

Papageorgiou, D. G., Kinloch, I. A. and Young, R. J., (2017). “Mechanical properties of graphene and graphene-based nanocomposites.” Progress in Materials Science, 90, 75-127.

Patel, J. S., Parik, K. B. and Darji, A. R., (2017). “Study on concrete using fly ash, rise husk ash and egg shell powder.” International Journal for Research in Applied Science and Engineering Technology, 5(2), 566-570.

Peng, H., Ge, Y., Cai, C. S., Zhang, Y. and Liu, Z., (2019). “Mechanical properties and microstructure of graphene oxide-cement-based composites.” Construction and Building Materials, 194, 102-109.

Pliya, P. and Cree, D., (2015). “Limestone derived eggshell powder as a replacement in Portland cement mortar.” Construction and Building Materials, 95, 1-9.

Prabakaran, K. and Rajeswari, S., (2009). “Spectroscopic investigations on the synthesis of nano-hydroxyapatite from calcined eggshell by hydrothermal method using cationic surfactant as template.” Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy, 74(5), 1127-1134.

Preda, N., Costas, A., Enculescu, M. and Enculescu, I., (2020). “Biomorphic 3D fibrous materials based on ZnO, CuO and ZnO-CuO composite nanostructures prepared from eggshell membranes.” Materials Chemistry and Physics, 240, 122205.

Qureshi, T. S. and Panesar, D. K., (2019). “Impact of graphene oxide and highly reduced graphene oxide on cement based composites.” Construction and Building Materials, 206, 71-83.

Rahman, A. F., Goh, W. I., Mohamad, N., Kamarudin, M. S. and Hatial, A. A., (2019). “Numerical analysis and experimental validation of reinforced foamed concrete beam containing partial cement replacement.” Case Studies in Construction Materials, 11, e00297.

Rao, M. A., (2020). “Rheology of fluid and semisolid foods: principles and applications.” New York: Springer US.

Rivera, E. M., Araiza, M., Brostow, W., Castaño, V. M., Díaz-Estrada, J. R., Hernández, R. and Rodríguez, J. R., (1999). “Synthesis of hydroxyapatite from eggshells.” Materials Letters, 41(3), 128-134.

Şahin, Y. and Köksal, F., (2011). “The influences of matrix and stone fibre tensile strengths on the fracture energy of high-strength concrete.” Construction and Building Materials, 25(4), 1801-1806.

Shiferaw, N., Hable, I., Thenepalli, T. and Ahn, J. W., (2019). “Effect of eggshell powder on the hydration of cement paste.” Materials, 12(15), 02483.

Silvestre, J., Silvestre, N. and De Brito, J., (2016). “Review on concrete nanotechnology.” European Journal of Environmental and Civil Engineering, 20(4), 455-485.

Siqueira, F. B., Amaral, M. C., Bou-Issa, R. A. and Holanda, J. N. F., (2016). “Influence of industrial solid waste addition on properties of soil-cement bricks.” Ceramica, 62(363), 237-241.

Sivakumar, M. and Mahendran, N., (2014). “Strength and permeability properties of concrete using fly ash (FA), rise husk ash (RHA) and egg shell powder (ESP).” Journal of Theoretical and Applied Information Technology, 66(2), 489-499.

Syafiq, A., Vengadaesvaran, B., Ahmed, U., Rahim, N. A., Pandey, A. K., Bushroa, A. R., Ramesh, K. and Ramesh, S., (2020). “Facile synthesis of transparent hydrophobic nano-CaCO 3 based coatings for self-cleaning and anti-fogging.” Materials Chemistry and Physics, 239, 121913.

Tiberti, G., Minelli, F. and Pizzari, G., (2015). “Cracking behavior in reinforced concrete members with steel fibers: a comprehensive experimental study.” Cement and Concrete Research, 68, 24-34.

Tiong, H. Y., Lim, S. K., Lee, Y. L. and Lim, J. H., (2018). “Engineering properties of 1200 kg/m lightweight foamed concrete with egg shell powder as partial replacement material of cement.” E3S Web of Conferences, 65, Article ID 02010.

Tonelli, F. and Masuelli, M. A., (2019). “Acacia caven gum studies of hydrodynamic parameters.” Evolution in Polymer Technology Journal, 2, 1-11.

TSI, (2016). “TS EN 196-1 - Methods of testing cement - part 1: determination of strength.” Ankara: Turkish Standard Institute.

Ujin, F., Ali, K. S. and Harith, Z. Y. H., (2017). “The effect of eggshells ash on the compressive strength of concrete.” Key Engineering Materials, 728, 402-407.

Uygunolu, T., (2011). “Effect of fiber type and content on..."
bleeding of steel fiber reinforced concrete.” *Construction and Building Materials*, 25(2), 766-772.
Vichaphund, S., Kitiwan, M., Atong, D. and Thavorniti, P., (2011). “Microwave synthesis of wollastonite powder from eggshells.” *Journal of the European Ceramic Society*, 31(14), 2435-2440.
van der Werff, J. C. and de Kruijf, C. G., (1989). “Hard-sphere colloidal dispersions: the scaling of rheological properties with particle size, volume fraction, and shear rate.” *Journal of Rheology*, 33(3), 421-454.
Xu, Y., Zeng, J., Chen, W., Jin, R., Li, B. and Pan, Z., (2018). “A holistic review of cement composites reinforced with graphene oxide.” *Construction and Building Materials*, 171, 291-302.
Yerramala, A., (2014). “Properties of concrete with eggshell powder as cement replacement.” *Indian Concrete Journal*, 88(10), 94-102.
Zhang, P., Li, Q. F., Wang, J., Shi, Y. and Ling, Y. F., (2019a). “Effect of PVA fiber on durability of cementitious composite containing nano-SiO$_2$.” *Nanotechnology Reviews*, 8(1), 116-127.
Zhang, P., Li, Q., Wang, J., Shi, Y., Zheng, Y. and Ling, Y., (2019b). “Effect of nano-particle on durability of polyvinyl alcohol fiber reinforced cementitious composite.” *Science of Advanced Materials*, 12(2), 249-262.