Scientific paper

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 CO_2 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; Balendran *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 nanoalumina (Li *et al.* 2006), nanosilica, nanotitania (Folli *et al.* 2012), and then reached a significant level with 1D-materials like carbon-nanotubes (Tíong *et al.* 2018; Kim *et al.* 2019). The studies have concluded that the addition of nanosilica in cement-based composites leads to the im-

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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; Papageorgio *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 ($CaCO_3$), 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 Mahendran 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 nanoformulation 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.*

(2012) 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. 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 nanoeggshell for the first time in mechanical analysis and 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 ($[\eta]$), the voluminosity (V_E), and the shape factor (υ) 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 $[\eta]$ 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).

$$[\eta] = \frac{\eta_{sp}}{C} = \frac{\eta_{rel} - 1}{C} = \frac{\frac{t}{t_0} - 1}{C} \tag{1}$$

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.

$$\eta_{sp}/C = [\eta] + k[\eta]^2 C \tag{2}$$

$$[\eta] = \upsilon V_E \tag{3}$$

$$\gamma = \frac{\eta_{rel}^{0.5} - 1}{C(1.35\eta_{rel}^{0.5} - 0.1)} \tag{4}$$

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).

$$\text{MPSD} = 100.\sqrt{1/(n-p)\sum_{i=1}^{n}((q_{e,meas} - q_{e,cal})/q_{e,meas})_i^2} \tag{5}$$

$$\text{HYBRID} = 100/(n-p)\sum_{i=1}^{n}(q_{e,meas} - q_{e,cal})_i^2/q_{e,meas} \tag{6}$$

$$\text{ARE} = 100/(n)\sum_{i=1}^{n}\left|\frac{q_{e,meas} - q_{e,cal}}{q_{e,meas}}\right| \tag{7}$$

where n is the number of data points, p is the number of parameters and $q_{e,meas}$, $q_{e,cal}$ 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.

Table 1 Mix proportions and nomenclature of mortar mixtures.

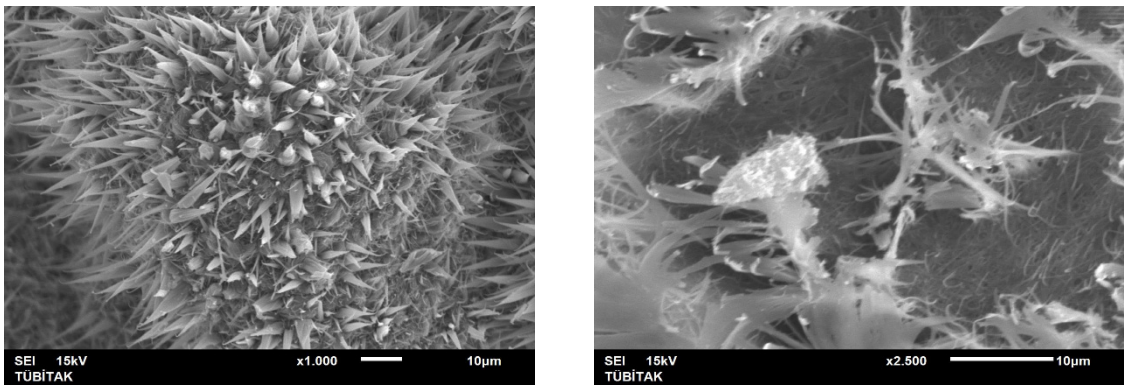
Mixture	NES (%)	NES (g)	Cement (g)	Sand (g)	Water (g)
Control	0	0	500	500	250.0
NES1	0.1	0.5	500	500	249.5
NES5	0.5	2.5	500	500	247.5
NES10	1	5	500	500	245.0

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}



(a) Magnification: 1000 (b) Magnification: 2500

Fig. 1 SEM images of nanoeggshell at different magnifications.

due to $CaCO_3$ (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 m^2/g. In the study of the conversion of waste eggshells to mesoporous hydroxyapatite nanoparticles was found high surface area (212.4 m^2/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 Kruif 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 (V_E) 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 (R^2). 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 (R^2) 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.

Table 2 Voluminosity and shape factors for nanoeggshell.

Time	V_E (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

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 (V_E) of sample decreased as the sonication time increased (**Table 2**).

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.

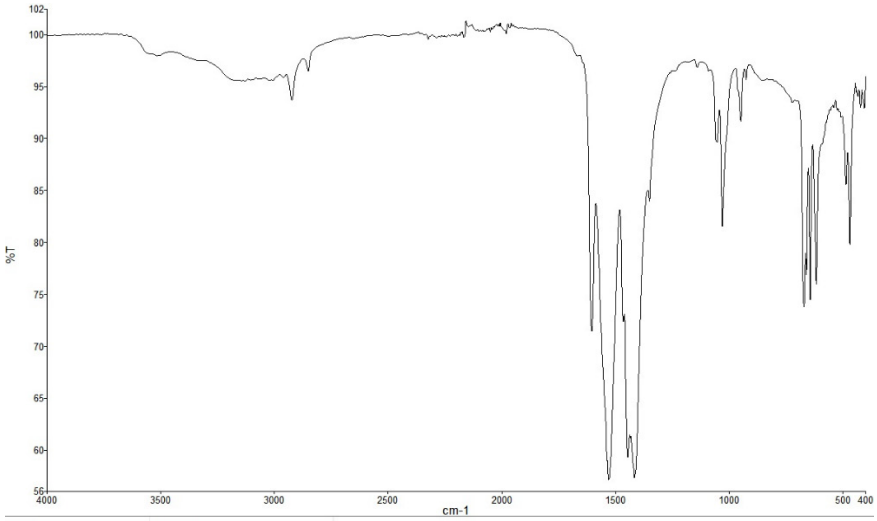


Fig. 2 FTIR spectrum of nanoeggshell.

Table 3 Huggins model by using the error analysis of the rheological properties of nanoeggshell.

Sonication time	Huggins Model		MPSD	ARE	HYBRID
10 min	$[\eta]$ (dl/g)	5.78	5.72	6.34	7.55
	k	2.68	2.73	3.14	3.88
	R^2	0.9979	-	-	-
30 min	$[\eta]$ (dl/g)	3.00	3.09	3.14	3.26
	k	8.44	8.56	9.35	10.17
	R^2	0.9972	-	-	-
1 h	$[\eta]$ (dl/g)	2.00	2.04	2.14	2.35
	k	15.00	15.16	16.34	17.56
	R^2	0.9999	-	-	-

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.

Table 4 Flow percentages of mortar mixtures.

Mixture	Nanoeggshell (%)	Flow (%)
Control	0	133
NES1	0.1	133
NES5	0.5	142
NES10	1.0	148

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

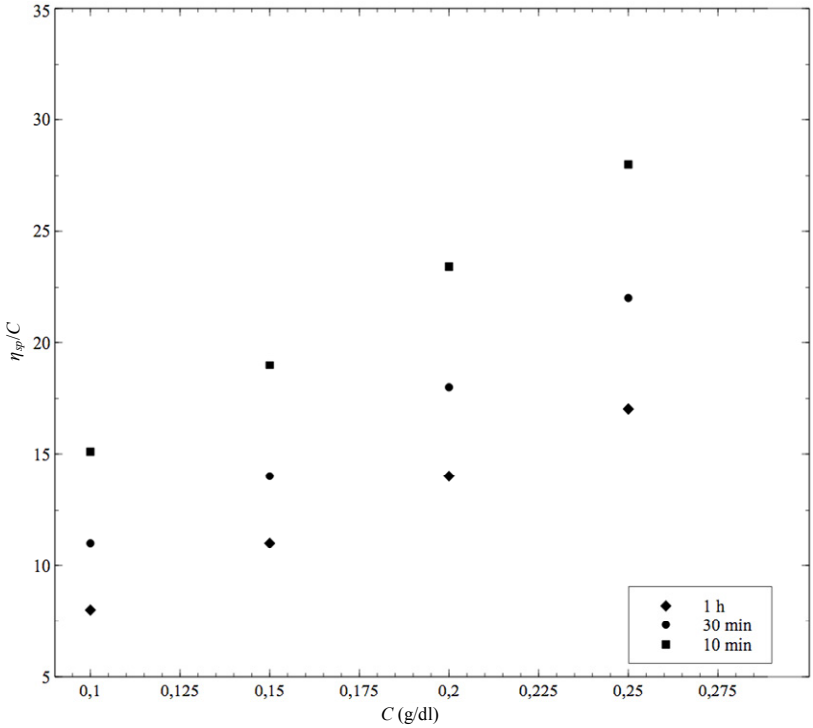


Fig. 3 Huggins models of nanoeggshell with different sonication time.

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

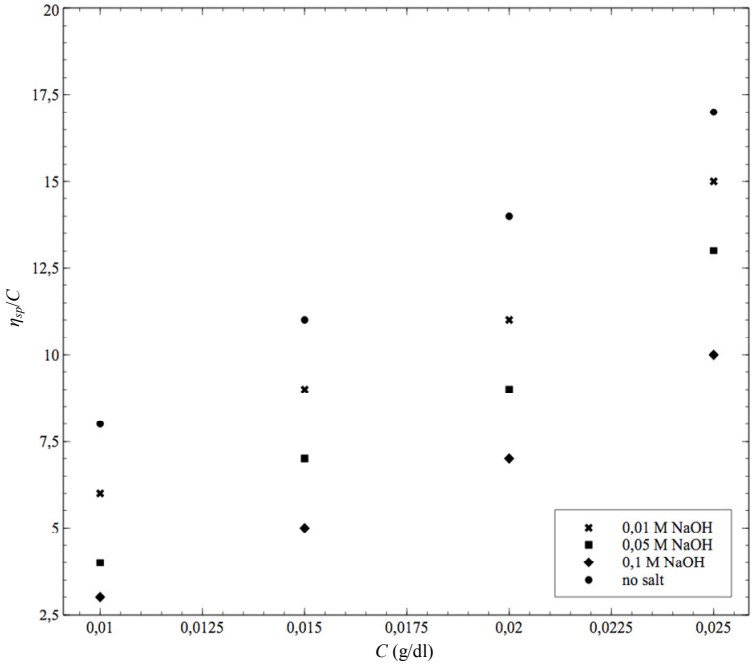


Fig. 4 Huggins models of nanoeggshell in different concentrations of NaOH.

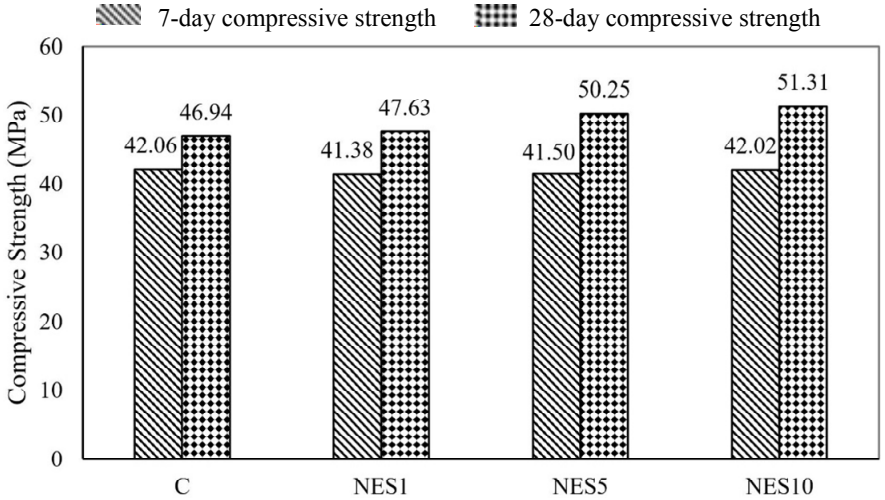


Fig. 5 7-day and 28-day compressive strength of specimens with different additive ratios.

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

Table 5 Average of maximum strain values under flexural loading.

Mixtures	ε_{av} (‰)
Control	3.41
NES1	4.02
NES5	5.41
NES10	5.75

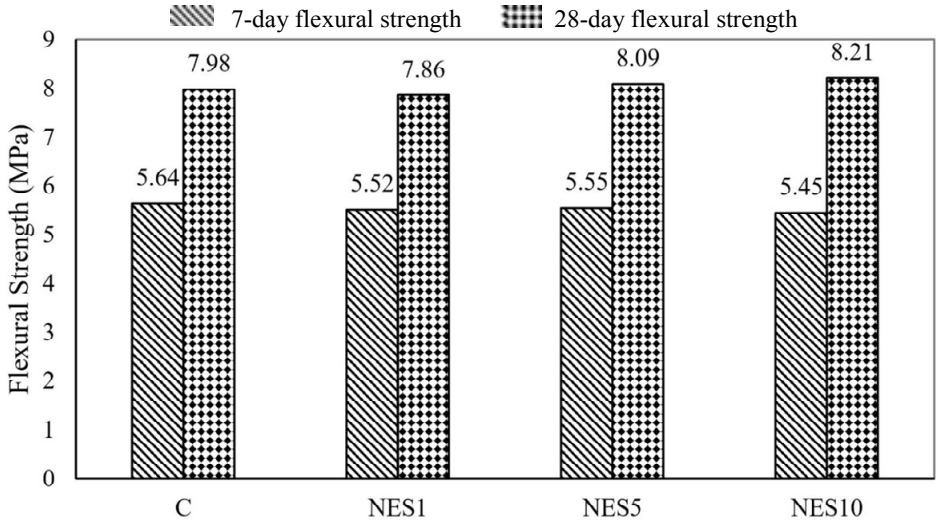


Fig. 6 7-day and 28-day flexural strength results of specimens with different additive ratios.

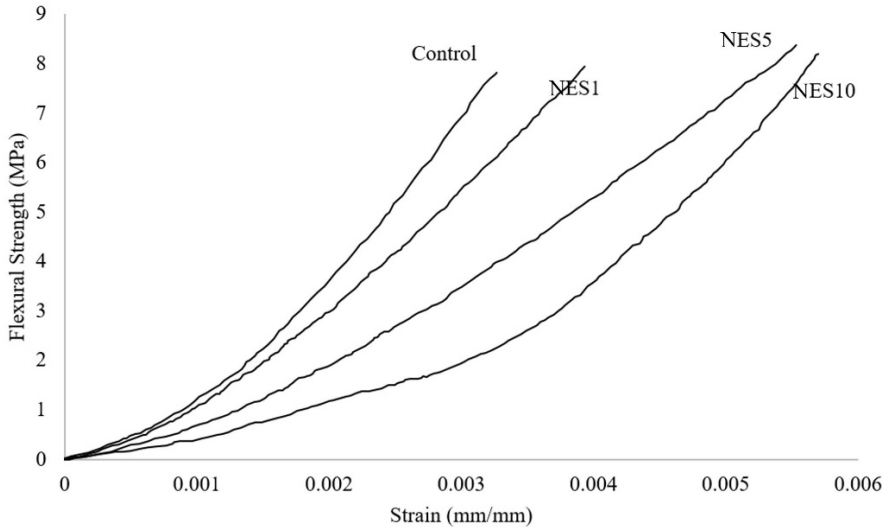


Fig. 7 Flexural strength versus strain curves.

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.

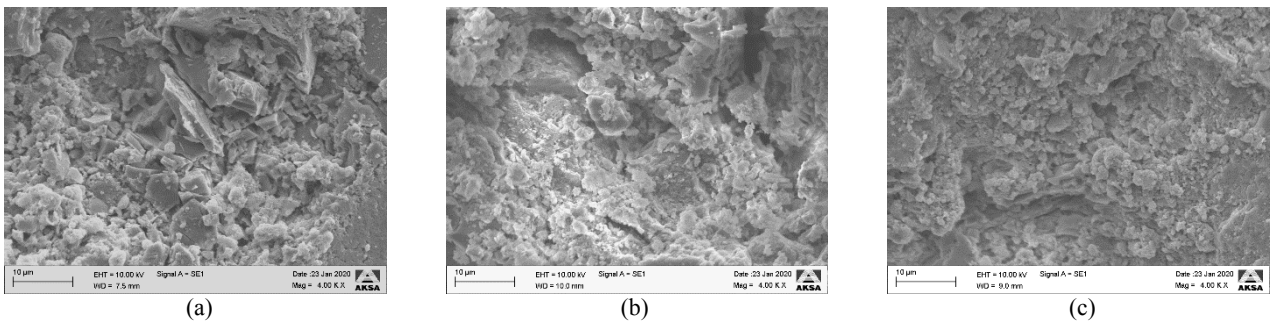
In previous studies on several nanomaterials, it is known that nanoparticles such as graphene oxide form strong interfacial bonding with the cement matrix if well dispersed (Lu *et al.* 2016; Chuah *et al.* 2014). Nanoeggshell exhibited good dispersion ability and very low aggregation when investigated 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 nanoeggshell was prepared using the microwaved-ultrasound-assisted method. The rheological properties and mechanical properties of nanoeggshell on cement mortar were investigated. First, the rheological properties of nanoeggshell 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 $CaCO_3$ was observed in nanoeggshell. According to the SEM images, the nanoeggshell had a 3D flower-shaped morphology with lengths below 100 nm of capillary arms. The surface area of nanoeggshell was 220.2 m^2/g and its specific gravity was 1.20.

In order to understand the effect of the solution form of 3D flower-shaped nanoeggshell in cement mortar mixture, four different cement mortar mixtures were prepared by adding the nanoeggshell 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 nanoeggshell in cementitious composites. The results of this study sup-



(a) (b) (c)

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.

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