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Alexandria Engineering Journal (2021) **xxx**, xxx–xxx

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A critical review of carbon nanomaterials applied in cementitious composites – A focus on mechanical properties and dispersion techniques

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Received 23 March 2021; revised 3 August 2021; accepted 20 August 2021

KEYWORDS

Carbon nanomaterials;
Dispersion;
Cost;
Dispersion measurement techniques;
Mechanical properties

Abstract This paper provides a current overarching review of several commonly used carbon nanomaterials applied within cementitious composites. It reviews the typical weight percentages used within mixes from several researchers in the field and assesses the application of these nanomaterials on the mechanical properties. Mechanical properties covered include compressive strength, flexural strength and tensile strength as well as elastic modulus. It was clear from this extensive but initial review that the dispersion methods and techniques used during mixing not only influenced the mechanical properties but also influenced the percentages of nanomaterials used in the mixes. This leads to a further review of dispersion methods and dispersion measurement techniques in order to gain insight into the best approach to take. The effect of dispersion methods on the quantities of nanomaterials used in mixes raised an interesting, last review on pricing comparisons (2020) and the development of a cost-to -weight ratio to better evaluate and compare between options from a cost perspective. Recommendations from this extensive review include; low percentage of graphene oxide provides better improvement compared with other carbon nanomaterials; Use of superplasticiser in mixes such as ADVA 210 to better aid dispersion; use of ultrasonication for a short cycle to improve dispersion; and finally, a mixed mode approach to the measurement of dispersion in mixes which includes scanning electron microscope (SEM) + ultraviolet–visible spectroscopy (UV–Vis) testing at solution phase + Mechanical properties after 28 days.

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Peer review under responsibility of Faculty of Engineering, Alexandria University.

https://doi.org/10.1016/j.aej.2021.08.053

Please cite this article in press as: M. Yaghobian, G. Whittleston, A critical review of carbon nanomaterials applied in cementitious composites – A focus on mechanical properties and dispersion techniques, Alexandria Eng. J. (2021), https://doi.org/10.1016/j.aej.2021.08.053

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1. Introduction

Cementitious composites are the most frequently used materials for infrastructure due to several reasons [1,2]. These materials are water-resistant and can easily be formed into numerous shapes and sizes. They also are cheap and available everywhere. Twice as much cementitious composites are used in infrastructures around the world than the total of all other building materials, including wood, steel, plastic, and aluminium [2]. Although cement-based composite materials such as concrete (and its many derivatives) demonstrate good mechanical performance in compression, generally, these materials exhibit low tensile and flexure strength. Cement composites have a quasi-brittle nature and cracks can easily appear and develop under tensile stresses [3-5]. One solution to overcome this weakness on the macroscale is to integrate fibres into the mixing phase to affect the long-term mechanical performance. Different types of fibres, such as carbon, glass and steel, to name but a few, can be introduced into the mixture to increase its ability to resist crack growth during service [6]. They can postpone the beginning of microcracks however they are not able to halt their initiation [7,4,8-10]. The reason is that spacing between fibres is large and microcracks can freely grow in the space between fibres before facing them [11,12]. Therefore, researchers have conducted studies about nanofibres in order to limit the initiation of cracking at the nanoscale. The most commonly used nanomaterials are nanoscale spherical particles (nano-SiO2, TiO2, Al2O3, Fe2O3etc.), nanotubes and fibres (carbon nanotubes and carbon nanofibers), and nanoplatelets (nano clays, graphene, and graphite oxide) [13,11].

This paper reviews the application of carbon nanomaterials into cement matrices and their influence on mechanical properties critically appraises studies found within the literature and makes recommendations on how to best integrate such nanomaterials in the future. It reviews the aforementioned nanomaterials applied in mixes and the percentages used, it reviews dispersion methods and techniques for measuring the effectiveness of dispersion and also reviews costs of the nanomaterials in the context of material used in a mix. A conclusion to draw from this current work is that the dispersion methods and techniques adopted are key in attaining consistent and improving mechanical properties. Another conclusion from this paper is that Graphene Oxide would be the one of the best suited nano-reinforcement materials for application in cement-based composites as they currently offer the best cost per used-material ratio for the related increase in mechanical properties. It is also evident from this review article that short length carbon nanomaterials offer better mechanical properties when used in cement composites, with the best practical range being between 1.5 μm to 30 μm. And finally AVAD210 can be considered as effective superplasticiser in dispersion of nanomaterials.

2. Initial literature review

Three main advantages should be considered when nanomaterials are used 1) production of high-strength cementitious composites (and by extension high strength concrete) for a particular application 2) reducing the amount of cement needed in concrete in order to obtain similar strengths and decreasing the cost and the environmental impact of construction materials and finally reducing the construction periods as nanomaterials can produce high-strength concrete with less curing time[14].

Due to their unique thermal, mechanical, chemical, electrical properties and good performance as reinforcement materials, several studies have been conducted by researchers [8,15].

Nanoparticles can act as heterogeneous nuclei for cement pastes, further accelerating cement hydration due to their high reactivity, as nano reinforcement, and as nano-filler, densifying the microstructure, thereby, leading to a reduced porosity[16].

Scanning electron microscope (SEM) shows the image of TiO2, nano-SiO2 surface in Fig. 1

Although nanoparticles like nano-silica (SiO2) can improve cement hydration due to its high specific surface area (300 m2/g), it is not able to stop nano-size cracks duo to low-aspect-ratio[17]. In addition, nanoparticles absorb water from concrete owing to their water absorption while cement hydration requires a large amount of water. As a result, drying shrinkage occurs[18]. Fig. 2 shows how the surface water of the concrete evaporates continuously.

Carbon nanofibers (CNFs) have a good modulus of elasticity in the range of Tera Pascals (TPa) and tensile strength in the range of Giga Pascals (GPa), and also they can provide unique electronic and chemical properties [15]. However, Hogancamp and his colleague showed that CNFs do not have a major impact on stiffness of the cement mortar [19]. Fig. 3 shows A clump of vapour-grown carbon nanofiber (VGCNF).

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure that was first discovered by a Japanese scientist called Iijima in 1991 when he observed the graphite product by arc evaporation [5]. CNTs are classified into two main categories: single-wall carbon nanotubes (SWCNTs) with a single graphene sheet rolled into a hollow

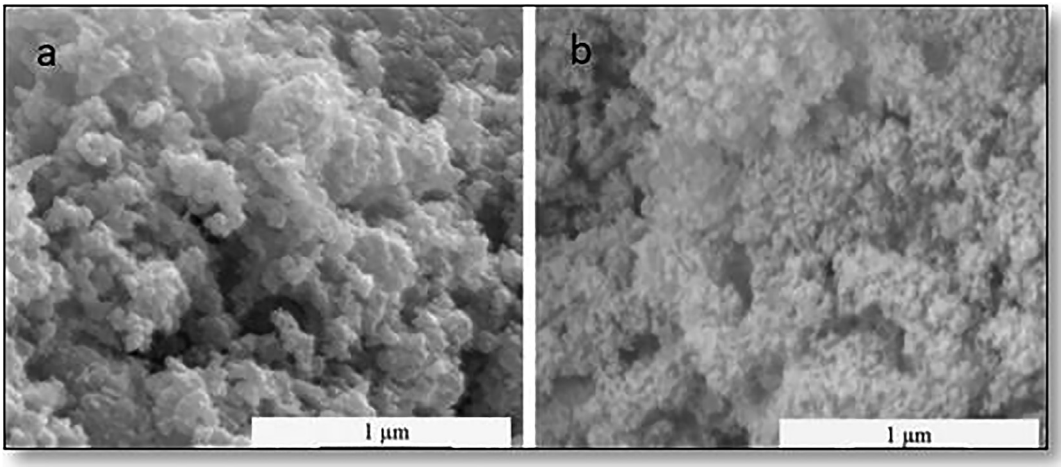

Fig. 1 Scanning electron microscopy (SEM) a) TiO2 b) nano-SiO2.

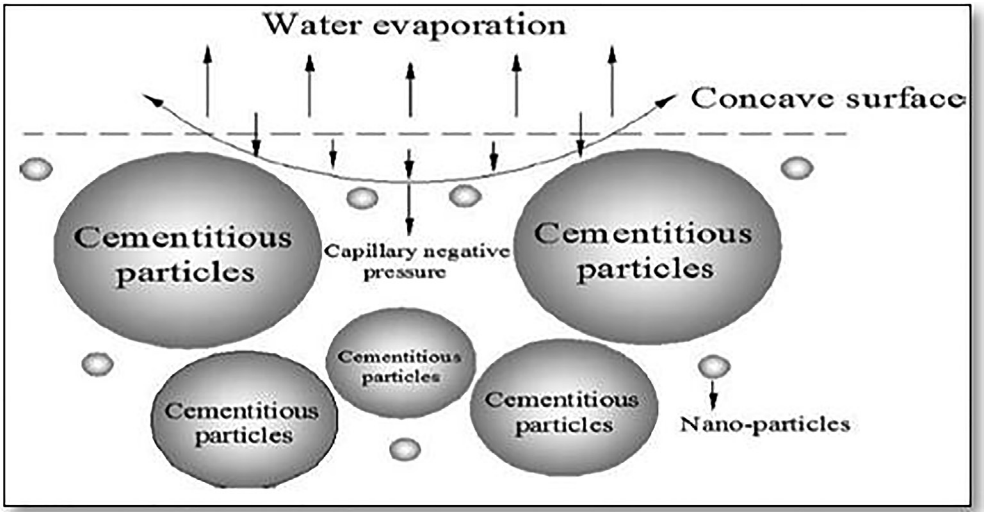

Fig. 2 *Force simulation of air–liquid meniscus* [18].

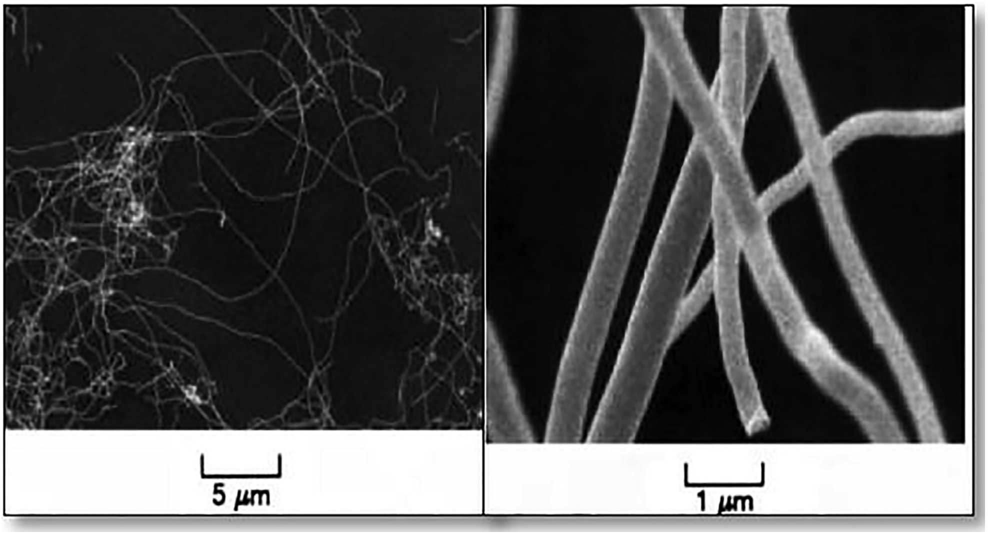

Fig. 3 *A clump of VGCNF* [20].

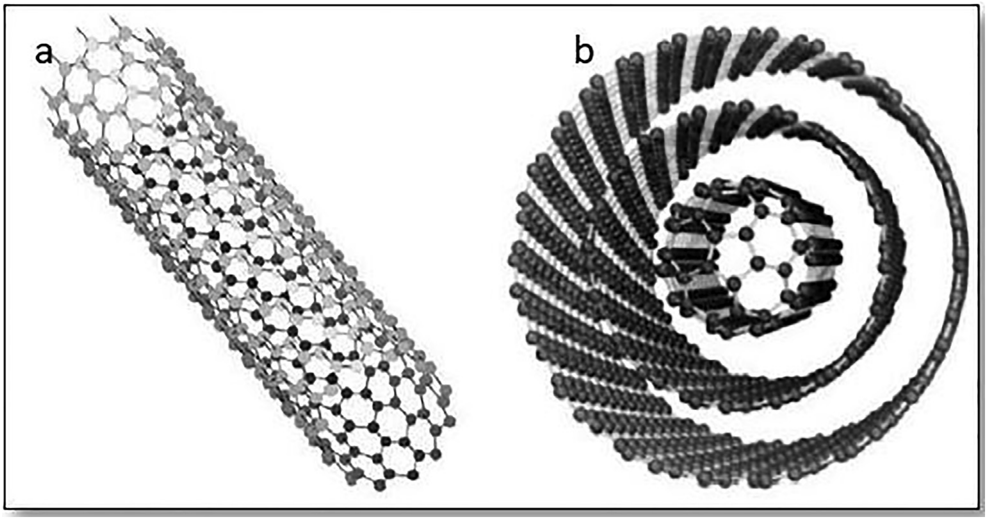

Fig. 4 *Schematics of CNTs a) SWCNTs b) MWCNTs* [26].

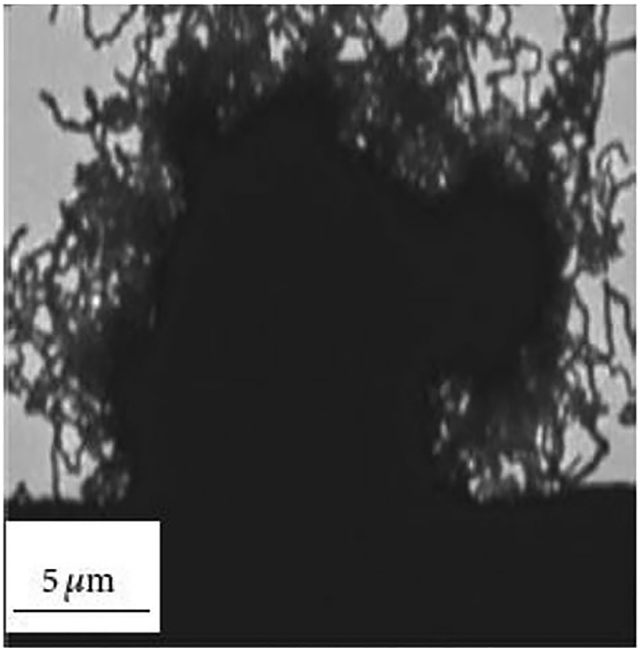

Fig. 5 *The TEM image of complete coverage of cement particles by MWCNTs* [32].

cylinder and multiwalled carbon nanotubes (MWCNTs) are composed of multiple, concentric graphene cylinders coaxially arranged around a hollow core [5,21,22,23,9,15,24,25]. Fig. 4 Shows the CNTs structure.

There are many ways to synthesize CNTs such as laser ablation, Solar Energy for Vaporization, Electric Arc Discharge, and Chemical Vapor Deposition (CVD) [27,28,29]. Since Arc-discharge and laser ablation methods consume lots of energy limitations are utilizing these methods [29,28]. the CVD method is generally known to be an easy and efficient process for CNT production [30,29,28]. Nanotubes grow as a gaseous carbon source, usually, a hydrocarbon decomposes on the catalyst particles and forms graphitic carbons with temperatures ranging from 873 to 1273°C [27].

Because of the high aspect ratio of CNTs, higher energy is needed for crack propagation compared to low aspect ratio fibre [23]. In addition, CNTs have excellent physical properties, such as high strength and Young's modulus that are 20 times and 10 times stronger than carbon fibres [5,25], However, researchers faced two main problems when using CNTs that includes a dispersion of the fibres in the cement paste and also bonding between cementitious materials with CNTs. Due to strong van der Waal's forces, CNTs tend to form agglomerates or bundles which are more likely to defect sites in the composites [31,9,17]. Fig. 5 shows the cement-based hybrid material consisting of CNTs attached to cement particles [32].

The second problem is the bonding between CNTs and the cement matrix. The reason being, a lack of interfacial areas between CNTs and the cement matrix, which means that the CNTs are easily pulled from the matrix when subjected to tensile stresses[31,9,17].

Graphene is a flat sheet of carbon atoms that creates a significant contact area with the cement [9]. Graphene is a monolayer of sp2 bonded carbon atoms that was first obtained by mechanical exfoliation of bulk graphite and by epitaxial chemical vapour deposition[33]. Indeed, Graphene oxide is graphite that has been oxidized to distribute the carbon layers with oxygen molecules and after that, decreased to separate the carbon layers into individual or few-layer graphene. The structure and properties of GO depend on the synthesis method such as Hummer's method, Brodie, Staudenmaier, modified Hummer's method, and degree of oxidation [34,35,36]. Since hummer's method remove toxin gas by replacing Potassium chlorate with Potassium permanganate ($KMnO_4$), it can improve the security of experiments. Another benefit of using hummer's method is reducing oxidation time [36]. Fig. 6 shows a schematic model of a graphene sheet.

The main products of graphene are Graphene nanoplatelets (GNP) Graphene nanosheets (GNS) Graphene oxide (GO) Reduced graphene oxide (rGO) [38]. Schematic model of GO, rGO, and GNPs can be found in Fig. 7.

GO consists of a hexagonal carbon network bearing hydroxyl, epoxide, carboxyl and carbonyl functional groups [40].

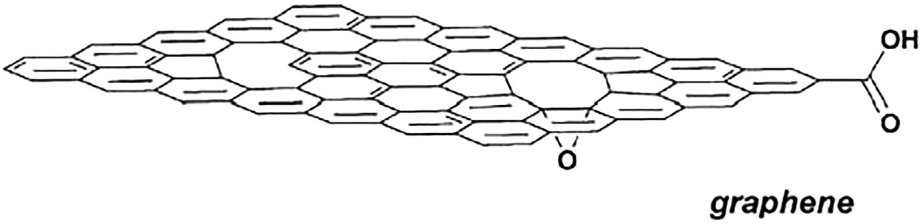

Fig. 6 *Schematic model of a graphene sheet* [37].

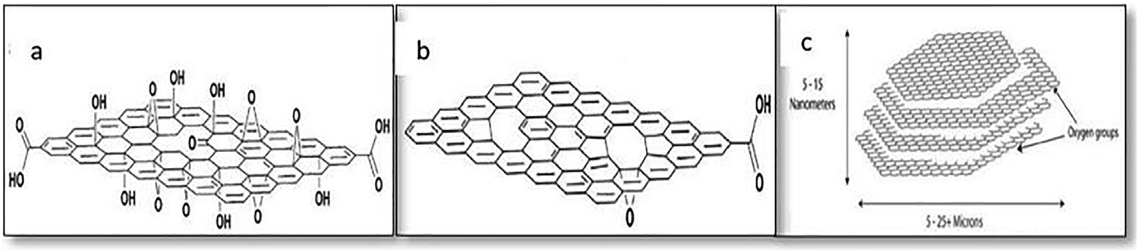

Fig. 7 *Schematic model of a) GO* [37] *b) rGO* [37] *c) GNPs* [39].

The oxygen functional groups, attached on the basal planes and edges of GO sheets, modify van der Waals interactions between the GO make it easily dispersed in water [40,9,4]. Moreover, GO shows high values of tensile strength, aspect ratio and large surface [9,17]. Another positive aspect of GO is that it can accelerate the hydration of cement and regulate the formation of hydration crystals, this leads to improving the mechanical strength of cement composite [4]. These three factors make GO an ideal material compared with other nanomaterials to use in cement composite. However, the structural defects of GO increase with the increase of oxygen content and can affect the unique structure of graphene. As a result, it reduces thermal conductivity and electrical conductivity. Hence, the preparation of graphene with suitable oxygen content is necessary[1].

GO has a wide range of applications such as functional fluids solar cells, polymer composites, cement composites, drug delivery systems, conductive films, biosensors, transistors, supercapacitors, nanocomposites, bio-materials, lithium ion battery, water treatment process, conductive polymers and conductive inks [41]. However, the scope of this study will focus on mechanical properties.

3. Review of mechanical properties of carbon nanomaterials

Different environments and various external loads can affect on mechanical properties of nanomaterials that play an important role in improving the performance of the cement composite. Several studies have been conducted to provide high performance of cement composites by changing the percentage of carbon nanomaterials replacing with the weight of cement (wt%). For example, Rashid K. Abu Al-Rub et al studied the effect of CNFs and MWCNTs in cement composite in a concentration of 0.1% and 0.2% by weight of dry cement and they used acrylic moulds with a size of 6.5 × 6.5 × 160 m m^3. The result showed that although the modulus of elasticity increased in the cement composite using both CNFs and MWCNTs, flexural strength dramatically dropped in 0.1 wt % of MWCNTs [21]. The reason was that the Authors used an acid treatment (sulphuric and nitric) that created Sulphate ions which led to localized debonding. As a result, the flexure strength of cement composite was reduced by about 44%.

Maria S. Konsta-Gdoutos et al investigated the effect of MWCNTs on the performance of cement composite. The authors used two different percentages of MWCNTS by adding 0.048 wt% and 0.08 wt% and used a combination of short and long lengths of MWCNTs in their study. They observed that the highest increase of Young's modulus is achieved with 0.048 wt% long lengths and 0.08 wt% short length of MWCNTs by 56.25% and 62.5% respectively. This conclusion indicated that it is probably a higher concentration of short MWCNTs that is needed to achieve effective reinforcement while a lower concentration of long MWCNTs is required to obtain the same increment in Young's modulus [42]. Similarly, Bo Zou et al stated that MWCNTs can improve flexural strength and modulus of elasticity by adding 0.038 wt% and 0.075 wt% of MWCNTs in cement composite [43]. In comparison between Maria S. Konsta-Gdoutos experiment and Bo Zou both achieved better Young's modulus and flexure strength when used a similar percentage of MWCNTs (0.08 and 0.075 respectively). Shilang Xu et al carried out investigations to determine the flexural strength and compressive strength of cement composite by adding 0.025 wt%, 0.05 wt %, and 0.1 wt% of MWCNTs. The results showed that the compressive strength improved by 6%, 13%, and 15% respectively. Besides, the flexural strength increased by 7.5%, 15%, and 30% [44]. Like other researchers, test results by Shilang Xu also showed that increasing the percentage of MWCNTs can lead to achieving a better result in the performance of cement composites.

Various researchers have investigated the effect of GO on the mechanical properties of cement composites. For instance, the effect of graphene oxide nanosheets on mechanical properties of cement composites was carried out by Shenghua Lv et al. who used 5 different percentages of GO in cement composites. They added 0.001 wt%, 0.002 wt%, 0.003 wt%, 0.004 wt%, and 0.005 wt% of GO. The compressive strength increased to 47.9% by adding 0.005 wt% of GO. Moreover, the results showed that tensile and flexural strength improved with increasing GO dosage up to 0.003 wt% by 78.6%. However, a further increment of GO dosage decreased the percentage of tensile and flexural strength slightly [3].

According to Li Zhao et al. the compressive strength and flexural strength of cement enhanced with adding 0.022% of GO by 18% and 23% respectively[45]. However, Xiangyu Li et al result is opposed to Li Zhao. They announced that adding 0.02 %of GO decreased the compressive strength of cement paste by 4%[46]. They stated that when the GO content is below 0.03%, GO incorporation can't improve the compressive strength of cement composite.

Yuan Gao et al combined CNTs and GO in cement composite. They added GO/CNT suspensions with 0.4 g and 0.2 g of CNTs and GO respectively into the dry cement powders and then poured into 20 mm × 40 mm × 160 mm steel moulds. They found that modulus of elasticity increased by 53% and flexure strength improved by 79% [47]. A similar experiment has been conducted by Cheng Zhou et al. They utilized MWCNTs(0.04 wt%) and GO(0.02 wt%) together in cement composite. they found that compressive strength and flexural strength improved by 23.9% and 16.7% respectively [48]. Baoguo Han et al carried out investigations to determine the flexural strength and compressive strength of cement composite by adding 0.02 wt%, and 0.01 wt% of multi-layer graphene's (MLGs). They used moulds with sizes of 20 mm × 20 mm × 40 mm for the compressive test and 40 mm × 40 mm × 160 mm for the flexural test. The results showed that the compressive strength improved by 54%, and the flexural strength increased by 21% [49]. Similarly, Sun et al experimented with the same percentage of MLGs in cementitious composites and the result showed the same improvement in compressive strength by 54% [50].

All the details above are summarised in Table 1 for the clarity of readers.

To appraise Table 1, the range of lengths that have been used for MWCNTs is between 5 μm to 100 μm. From this table, the range of water-cement ratio is between 0.33 and 0.5 and the range of CNTs is incorporated to cement composite is between 0.038 wt% and 0.2 wt%.

Maria S. Konsta-Gdoutos et al could obtain the best elastic modulus and flexural improvement among other researchers by adding 0.08 wt% of CNTs. They also used a short length of MWCNTs. Similarly, Bo Zou et al used a short length of MWCNTs and almost the same percentage of MWCNTs that Konsta-Gdoutos used (0.075 wt%) and achieved the best flexure strength in the cementitious composite.

The table shows the range of water-cement ratio used by researchers for GO is between 0.36 and 0.4. The range of GO percentage is much less than the percentage of CNTs between 0.001 wt% and 0.04 wt%. This is an interesting point, as less GO is needed for a marked improvement than for CNT's. Besides, the improvement of cement composite was much better than CNTs. The best result of GO incorporation in compressive strength in this table achieved by 0.005 wt% of GO around 48%.

With reference to Table 1, a general comparison between GO and CNTs highlights that GO showed a better improvement in the mechanical properties of cement composites. The best improvement of CNTs (0.075 wt%) in flexure strength was about 50% while adding a much less percentage of GO (0.003 wt%) improve the flexure strength of cement composite by almost 61%. Furthermore, Table 1 shows multi-layer graphenes have a huge improvement in compressive strength of cement composite by 54% that slightly higher than GO by 47.9%.

According to the results obtained from Table 2, the best percentage of MWCNTs that can achieve to improve cement composite is 0.08 wt% and the best percentage of GO that can optimise the performance of cement composite is between 0.003 wt% and 0.005 wt%. Table 2 presents the best mechanical properties of cement composites achieved by nanomaterials.

From the above discussion, a sensible conclusion to draw would be; it appears that dispersion techniques/methods can influence mechanical performance. A discussion about the dispersion of carbon nanomaterials in cement composites now follows.

4. Review of dispersion of carbon nanomaterials in cement composites

Due to the strong van der Waals force of nanomaterials, the distribution of nanomaterials is very difficult in cement composite. This force results in the formation of agglomerations and makes it difficult to disentangle[53]. Fig. 8 shows a poor interfacial bond between the CNFs and matrix in several areas of the material with many cavities.

To follow on from previous research reviewed above on the significance of nano-material length, Yazdanbakhsh et al did an investigation on the effect of length on dispersion. Compared with the size of nanomaterials, cement particles are very large, which leads to size compatibility issues. The reason is that nanomaterials cannot penetrate in the area of cement grains. As a result, some other areas have more concentration of nanomaterials that it is more likely to have clumping of nanomaterials and consequently poor dispersion[53]. Moreover, inadequate dispersion results in unreinforced regions which allows crack propagation. As a result, poor dispersion can have an adverse effect on mechanical properties of cement composites and decrease tensile, compressive, and flexural strengths. Hence, dispersion plays an important role in the mechanical properties of cement composites.

5. Dispersion of carbon nanomaterials in cement pastes

Two main techniques can be utilized for dispersing Carbon nanomaterials in an aqueous solution or water. First mechanical dispersion methods such as high shear mixing and ball milling, separate Carbon nanomaterials from each other or ultrasonication method which is a popular method among researchers. The second approach for dispersion of Carbon nanomaterials is designed to modify Carbon nanomaterials surface structures in two ways, physically that surfactants alter the non-covalent surface or chemically (covalent surface modification) [54]. On the other way, the dispersion problem can be solved by using surfactants or sonication or combining both methods [1]. GO can be well dispersed in water, however, dispersion of GO in cement has been restricted due to the electrostatic interaction with charged ions in cement pore solution[4].

Table 1 Performance of CNTs, CNFs, and GO in cement composite.

Researchers	Carbon nano materials	Length(L)/Diameter(D) Thickness(T)	w/c	wt%	Mechanical property improvement			
					Compressive	Tensile	Module of elasticity	Flexure
Maria [42]**S. Konsta-Gdoutos**	MWCNTs(short)	D20-40 nm/*L*10-30 μm	0.5	0.048			27.5%	17.5%
		D20-40 nm/*L*10-30 μm	0.5	0.08			62.5%	25%
	MWCNTs(long)	D20-40 nm/*L*10-100 μm	0.5	0.048			56.25%	25%
		D20-40 nm/*L*10-100 μm	0.5	0.08			5%	25%
Yuan Gao [47]	CNT mix withGO	*L*10–20 μm/D5–15 nm D500nm–5 μm/T0.8–1.2 nm	0.4				53%	79%
Shenghua Lv [3]	GO	T0.8 nm/D80-260 nm		0.001	13.4%	47%		51.7%
				0.002	27.6%	59.5%		32.9%
				0.003	38.9%	78.6%		60.7%
				0.004	42.2%	36.6%		30.5%
				0.005	47.9%	35.8%		30.2%
Bo Zou [43]	MWCNTs	D9.5 nm /L1.5 μm	0.4	0.038			13%	25.13%
				0.075			31.54%	49.89%
Cheng Zhou [48]	GO suspension		0.4		23.9%			16.7%
	MWCNTs	D30-50 nm		0.04				
Rashid [21] **K. Abu Al-Rub**	CNFs	D60- 150 nm/L30–100 μm	0.4	0.1			2%	55%
				0.2			23%	14%
	MWCNTs	D9.5 nm/L1.5 μm		0.1			6%	−44%
				0.2			22%	33%
Shilang Xu [44]	MWCNTs	D40-80(nm)/L5-15 μm	0.33	0.025			6%	7.5%
				0.05	13%			15%
				0.1	15%			30%
Li Zhao [45]	GO		0.42	0.022	17.68%			22.55%
Xiangyu Li [46]	GO		0.4	0.02	−3.80%			
				0.03	7.70%			
				0.04	14%			
Baoguo Han [49]	MLGs	T1-5 nm	0.3	0.02	54%			
			0.6	0.01				21%
Shengwei Sun [50]	MLGs	T1-5 nm	0.03	0.03	5.5%			
				0.02	54%			
				0.01	10%			
Zeng-shun Chen [51]	GO mixed withcarbon-fibre		0.4	0.004	24.95%			20.48%
				0.006	23.89%			
				0.01	46.9%			43.59%
Hui Peng [35]	GO		0.35	0.03				21.86%
				0.01	5.6%			
Jintao Liu [52]	Graphene sheets		0.4	0.01	13.5%			
				0.025	10%			16%

Table 3 and Table 4 shows that most of the researchers have used sonication and superplasticizer (SP) at the same time. Fig. 9 shows an ultrasonic processor that has been popular among researchers [47,55,46].

The most common method is dispersing the nanomaterials with sonication and a surfactant such as a superplasticizer. Fig. 10 shows a generalized chemical structure for the SPs.

Dispersion of GO is usually a combination of surfactants like Gum Arabic, Micro air 905, Sika Viscocrete 6 and ADVA 210 and mild sonication in an aqueous solution [40].

Another method to improve the dispersion of nanomaterials in cement composite is to distribute and attach them to the surface of cement particles before hydration. Then the slurry was dried and ground to form a powder. Powder's image showed that grains of cement powder are coated by CNTs bundles [53].

During sonication, ultrasonic waves are usually transmitted from a probe into a liquid and produce alternate expansions and compressions. The pressure fluctuations make cavities, which expand during the negative pressure excursions and implode violently during the positive excursions. As the bubbles collapse, millions of shock waves, acoustic streaming, and a combination of pressure and temperature extremes are generated at the implosion sites. The cumulative amount of energy produced is extremely high and significantly accelerates chemical reactions and breaks the clumps and agglomerations of particles[53,31]. Fig. 11 illustrates that CNFs agglomeration in several areas without sonication (picture a) and only 15 min of sonication improve the dispersion and CNFs distribute equally in aqueous media (picture b)[31].

However, long time sonication can reduce sheet size and introduces defects that decrease nanomaterials properties[58].

Table 2 The best mechanical properties of CNTs and GO obtained by researchers from table 1.

	Length μm	w/c	wt%	Mechanical properties improvement			
				Compressive	Tensile	Modulus of Elasticity	Flexural
CNTs	10–30	0.5	0.08			62.5%	
	1.5	0.4	0.075				49.89%
GO	0.0008–0.0012	0.36	0.005	47.9%			
			0.003		78.6%		60.7%
MLGs	0.3		0.02	54%			

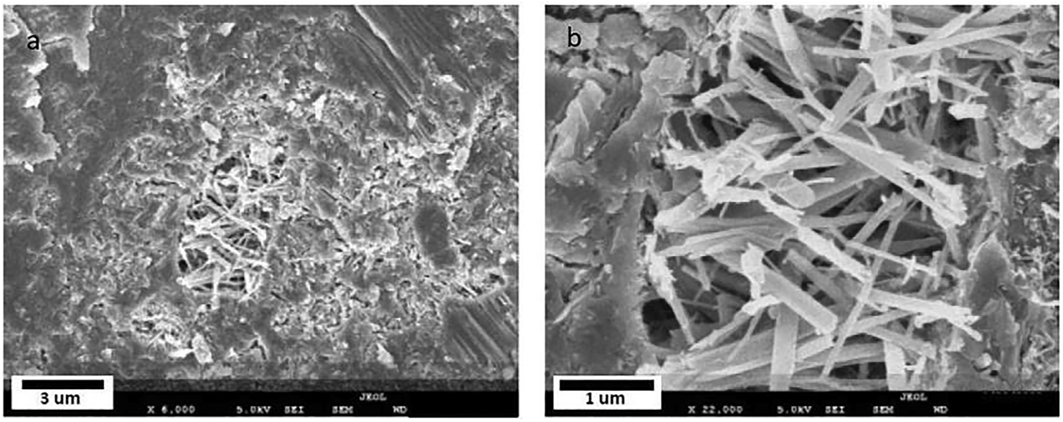

Fig. 8 *A clump of CNFs within a pore in the hardened cement paste and both pictures are taken from the same location in two different scales* [31].

Fig. 12 shows how a long period of sonication breaks and shorten CNFs[31].

5.1. Methods for measuring effective dispersion

Several investigations have been done on the dispersion stability of carbon nanomaterials by using different methods such as electron microscopy (TEM and SEM) [3,42,59,60,44,61,62] , atomic force microscopy (AFM) [3] ,Raman spectroscopy (RS) [61], ultraviolet–Visible (UV–Vis) spectroscopy [40,62,3] and dynamic light scattering . The most common method of appraising the distribution of nanomaterials in a composite is scanning electron microscopy (SEM). The SEM image relies on surface processes and has a great depth of field depending on the instrument design and settings. It can produce images that are good representations of the three-dimensional shape of the sample[63]. SEM is the only method that shows the actual distribution of nanomaterials in the hardened matrix, while the other methods evaluate dispersion in the water used for producing cement Paste [31]. Transmission Electron Microscopy (TEM) technique rely on the wavelength of the electron beam as the critical factor responsible for ultimate resolution [28]. In this method, image is formed from the interactions of electrons transmitted in the form of a beam through a very thin specimen. Since the sample should be solid, the dispersion is usually frozen quickly and maintained at cryogenic temperatures (−196 °C) in the form of amorphous ice [31].

Scanning probe techniques such as AFM are extensively employed to characterize thin sheets of layered materials and they can directly image the surface topography of the sample [54,64]. There are four underlying sources of image artifacts in AFM methods: probes, scanners, image processing, and vibrations. The probe connects to the surface directly and the resulting probe deflection can be measured by optical methods to generate an image[28]. However, some authors mentioned some issues using AFM. The procedure of AFM itself is delicate and needs experts to handle it [29]. Moreover, AFM suffers from slow scan speed, small scan area, low throughput, and needs good isolation against noise [29,65]. Besides samples need to be delivered on smooth substrates such as silicon wafer, quartz, freshly cleaved mica and the presence of surfactant on the substrate makes AFM characterization difficult [61]. Another problem can be the movement of the tip on the sample and the movement can occur vertically and also along the cantilever axis, which limits the validity of applied contact mechanics [28].

Raman spectroscopy also can be utilized to characterize carbon nanomaterials [64,65,66]. This technique is popular Since it does not need a low temperature or vacuum. Information about the presence of defects, strain, nature of the bonding, number of layers in the case of graphene, and diameter in CNTs can be achieved by Raman spectroscopy [64]. However, Raman image required use of a focused laser beam that can damage the sample of nanomaterials [29].

Table 3 Summery of different researches of dispersion of CNTs.

Researchers	Carbon nano materials	Length(L) Diameter(D) Thickness(T)	w/c	wt%	Dispersion in	Chemical treatment	Mechanical treatment	Dispersion measurement
Maria [42]S. Konsta-Gdoutos	MWCNTs	L (10-100µm)	0.5	0.048	cement composite	surfactant	Ultrasonication 1500-2100J/min	SEM
			0.5	0.08				
Peng-Cheng Ma [59]	CNTs	D (10–20 nm) L(10-50)			Water	dimethylamino-pyridine 100mg Dicyclohexylcarbodiimide 800mg Toluene 50mg	Ultrasonication 60 minutes	TEM SEM
Frank Collins [60]	MWCNTs	D(10–100 nm) L(5–15 µm)	0.4	0.5	Cement composite	Styrene butadiene rubber co-polymer	Ultrasonication (150w)(12 min)	SEM
			0.4	0.5		alkylbenzene		
			0.4	0.5		Aliphatic propylene glycol ether		
			0.5	1		Polycarboxylate		
			0.5	1		Calcium naphthalene sulfonate		
			0.6	2		Naphthalene Sulfonic Acid		
			0.6	2		Lignosulfonate		
Bo Zou [43]	MWCNTs	D9.5 nm	0.4	0.038	Cement composite	ADVA 210	Ultrasonication	SEM
		L1.5 µm	0.4	0.075				
Shilang Xu [44]	MWCNTs	D40-80(nm)	0.33	0.025	Cement composite	TNWDIS	Ultrasonication/ Centrifugation 600 W/2000 rpm	SEM
		L5-15(µm)	0.33	0.05				
			0.33	0.1				

Table 4 Summery of different researches of dispersion of GO.

Researchers	Carbon nano materials	Length(L) Diameter(D) Thickness (T)	w/c	wt%	Dispersion in	Chemical treatment	Mechanical treatment	Dispersion measurement
Mustafa Lotya [61]	GO				Water 5 mg/mL	Water-sodium cholate solutions	mild sonication centrifugation 24h (500–2000 rpm)	TEM SEM RS
Samuel Chuah [40]	GO		0.4	0.03	Cement composite/Water	Sodium hydroxide (NaOH)10.5PH	Sonication wavelength 190–1100 nm	UV-vis
			0.4	0.3		Potassium hydroxide (KOH)10.5 PH		
			0.4	0.3		Sodium chloride (NaCl2)0.01 mg/mL		
			0.4	0.3		Calcium chloride (CaCl2)0.01 mg/mL		
			0.4	0.3		Polycarboxylate (Viscocrete 6 and ADVA 210) 0.5 wt%		
			0.4	0.3		Micro air 905 0.5wt%		
			0.4	0.3		Gum Arabic0.5wt%		
Hongjian Du [62]	GNP	D8 μm T37nm	0.5		Cement composite	Polycarboxylate Superplasticizer(ADVA-181 N)	Ultrasonication 300w/20 kHz	SEM UV-vis
Shenghua Lv [3]	GO	D80-260 nm T0.8 nm	0.001 0.002 0.003 0.004 0.005		Cement composite	Polycarboxylate Superplasticizer	Ultrasonication 325 W AFM	UV–vis SEM

Dynamic light scattering (DLS) is a technique that measures the light scattered from the laser that passes through a colloid. A drawback of this method is that the detection of smaller nanoparticles in the presence of several percent of bigger ones seems to be very difficult and deliver poor result with smaller nanoparticles [67,68].

Another common method of measuring dispersion in a transparent medium is ultraviolet–visible spectroscopy (UV–Vis). This method is based on the colour of nanoparticles. The darker is liquid the better dispersion has achieved[31]. Fig. 13 shows three samples of CNFs with the same w/c ratio and the same parentage. In picture (a) CNFs were mixed with water only by hand stirrer which led to poor dispersion and high transparency while in the specimen (c) CNFs were sonicated which resulted in a good and dark dispersion[31].

Numerous studies have been reported about the dispersion of carbon nanomaterials. For example, Peng-Cheng Ma et al studied dispersion, interfacial interaction and re-agglomeration of functionalized carbon. They dispersed CNFs in water by adding organic amine such as dimethylamino-pyridine, dicyclohexylcarbodiimide, and toluene with ultrasonication for about 60 min. The result showed the attachment of amine molecules effectively prevents the re-agglomeration of CNTs[59].

Collins et al studied the influences of admixtures on the dispersion, workability, and strength of carbon nanotubes. They used numerous different dispersants/surfactants to improve the dispersion of CNTs. They added Styrene-butadiene rubber copolymer latex (SBR), alkyl benzene sulfonic acid, Aliphatic propylene glycol ether including ethoxylated alkyl phenol, Polycarboxylate, Calcium naphthalene sulfonate, Naphthalene Sulfonic Acid Derivative, and Lignosulfonate as aqueous solutions with ultrasonication. They reported that Following ultrasonication, polycarboxylate and lignosulfonate admixtures provided good dispersion of CNTs in aqueous solutions. However, Styrene-butadiene rubber and calcium naphthalene sulfonate admixtures facilitated rapid agglomeration of CNTs [60]. This is probably due to cross-linkers present in these solutions, especially in SBR. Similarly, Bo Zou et al investigated the dispersion of CNTs. They used ADAV210 as chemical treatment and ultrasonication to disperse MWCNTs. They used 5 different ultrasonic energy 25,75,150,250, and 400 J/mL. During sonication, the suspensions were placed in a water–ice bath to stop the temperature from rising. For measuring the effect of ultrasonication on the dispersion of CNTs they used UV–vis (only dispersed nanotubes can well absorb light in the UV–vis region) and optical microscope observations. Their experiment showed that 25 J/mL ultrasonication led to poor dispersion. By increasing the ultrasonication to 400 J/mL the dispersion improved[43]. Fig. 14 shows the differences between 25 J/mL and 400 J/mL ultrasonication.

Rashid K. Abu Al-Rub et al added water-reducing ADVA Cast 575 and nitric acid as a chemical treatment for dispersing MWCNTs and CNFs in cement paste. They discovered that CNFs and CNTs were well dispersed within aqueous solutions with the help of a chemical surfactant and ultrasonic mixing [21].

Konsta-Gdoutos et al used a 500 W cup-horn high intensity ultrasonic processor with a cylindrical tip and temperature controller for dispersing MWCNTs in cement composite. They also used two methods to examine the morphology and the microstructure of the fracture surface of MWCNTs by scanning electron microscopes and Secondary electron (SE) imaging. The result showed that for proper dispersion ultrasonic energy is necessary. They also found that the optimise weight ratio of surfactants to MWCNTs is almost 4 [42].

Shilang Xu et al used both sonication (20 kHz,600 W) and centrifugation (2000rmp) to disperse MWCNTs in cement composite. they found that the length of MWCNTs reduced from 5 to 15 µm to < 10 µm. it's more likely that the dispersion process damage CNTs[44].

Fig. 9 *500 W and 750 W ultrasonic processor* [56].

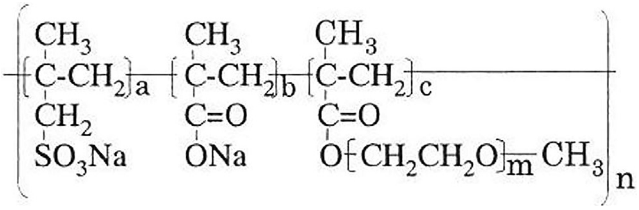

Fig. 10 *Generalized chemical structure for the range of synthesized SPs* [57].

Mustafa et al studied about high-concentration, surfactant-stabilized graphene dispersions. They used water-sodium cholate solutions(0.3 mg/ml) as a chemical treatment for dispersing GO in water and mild sonication (240 h) and centrifugation (500–2000 rpm). The result showed that the dispersions can be easily cast [61].

Samuel Chuah et al added several surfactants to disperse GO in cement composite and water. The admixtures were polycarboxylate, air entrainer and Gum Arabic. UV–vis and visual observations outcome suggested that one type of polycarboxylate which is known as ADVA 210 should add to cement composite before adding GO into it. ADVA 210 can disperse GO better in the pore solution environment, which is desirable to preparing GO-ADVA 210 suspensions [40].

In this chapter, to avoid duplication, only some researches with interesting points have been discussed in Table 3 and Table 4. More researches about the dispersion of nanomaterials can be found in Table 3and Table 4.

As Table 3 and Table 4 show, different researchers used different sonication frequencies. The reason is that various dosages of nanomaterials need different sonication energy to improve dispersion. As Bo Zou et al experiment showed that when they doubled the percentage of CNTs to 0.075 wt% the optimum ultrasonication shifts from 75 J/mL to 150 J/mL[43].

The frequency that is used by several researchers is between 55 W and 750 W due to different surfactant and nanomaterials dosage and time of sonication that it is various between 12 min to 240 h. Although in Table 3 and Table 4 all researchers used sonication, long sonication can have little improvement in dispersion and excess sonication power can lead to a deterioration of dispersion. As Gao et al experiments showed, dispersion of nanomaterials increases until 20 min of sonication and after 20 min the improvement of sonication was insignificant[47]. They also conducted a test about the power of sonication and their result showed that increasing energy from 73 W to 87 W improves the degree of dispersion to 90%. Furthermore, they proved that increasing the power of sonication can reduce the improvement of dispersion especially when the power reached 118 W[47].

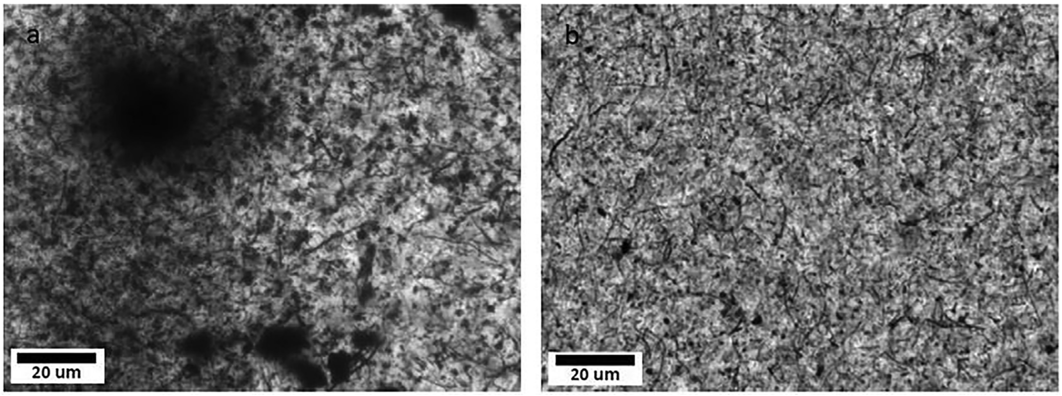

Fig. 11 *Effect of sonication on the dispersion of CNFs in aqueous media. Specimen a was only had-shaken but specimen b was sonicated about 15 min* [31].

6. Critical appraisal

From Table 1, Table 3, and Table 4 can conclude several main factors that can affect mechanical properties and dispersion. Firstly, the length of nanomaterials can play an important role in the improvement of the mechanical properties of cement composites. All researchers who used a short length of CNTs could have had better improvement in the mechanical properties of cement paste. Konsta-Gdoutos et al show that CNTs of shorter length can be more effective than a long length of

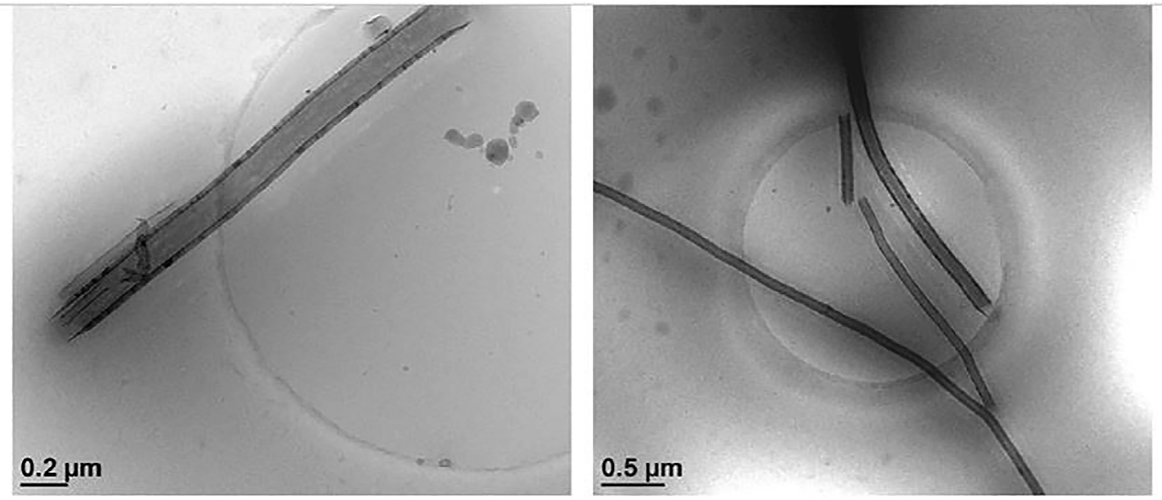

Fig. 12 *TEM images of CNFs. These fibres have been sonicated for 15 min and their aspect ratios are smaller than those that are not sonicated* [31].

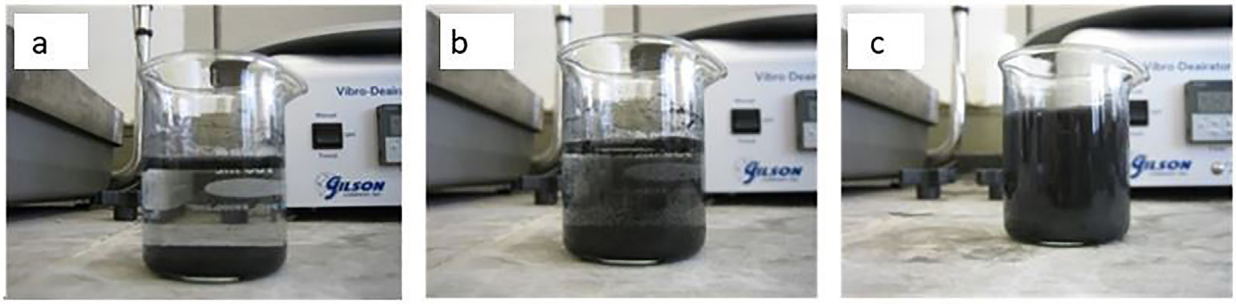

Fig. 13 *Effect of CNFs dispersion quality on the transparency of solutions. In sample (a) only a hand stirrer used for mixing CNFs in water which led to poor dispersion and high transparency. In specimen (b) surfactant added and again mixed by hand stirrer. Although the result showed better and darker dispersion, the sample is unstable, and dispersion is not equally through the water-surfactant solution. In specimen (c) sonication method had replaced with a hand stirrer and resulted in good and very dark dispersion* [31].

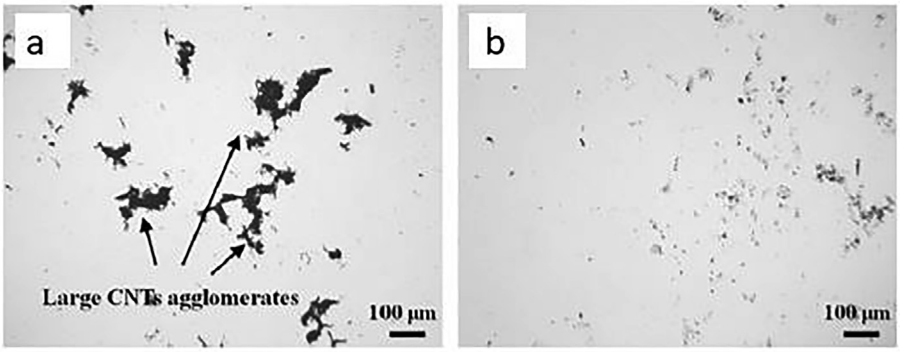

Fig. 14 *Optical microscope image of CNTs suspensions. picture a shows ultrasonication 25 J/mL b)400 J/mL* [43].

CNTs when considering flexural strength and modulus of elasticity[42]. The range of short lengths that all researchers used to improve the mechanical properties is from 1.5 µm to 30 µm. The reason is that long length nanomaterials probably have more chance to agglomerate due to their long length and much more effort need to deagglomerate nanomaterials bundles. Moreover, in the other fields, like conventional fibre composite materials, Daohai Zhang et al investigated the relationship between the long length of glass fibre and dispersion. The result showed that dispersion of long length (16 mm and 20 mm) is much harder than fibres with 4 mm and 8 mm and reduced mechanical properties[69]. Capela et al performed an investigation on the effect of carbon fibre length on mechanical properties of high dosage carbon reinforced. In this test, the stiffness increased when 4 mm of carbon fibre was used and when 6 mm carbon fibre was added to matrix stiffness decreased. Their SEM analysis showed that when 4 mm fibre length increased to 6 mm dispersion became

Table 5 Price of nanomaterials September 2020.

Nanomaterials	Outside diameter	Price	Convert to $	Supplier Website	Supplier Country
MWCNTs 95% (CCVD)	8 nm	$15/g		www.cheaptubes.com [71]	USA
MWCNTs 95% (CCVD)	8–15 nm	$15/g			
MWCNTs%95(CCVD)	10–20 nm	$15/g			
MWCNTs %95(CCVD)	30–50 nm	$10/g			
MWCNTs %95(CCVD)	50 nm	$10/g			
reduced GO		$200/g			
GNP		$15/g			
COOH Functionalized GNP		$30/g			
GO 99% (hummer method)2-4layer		$150/g			
GO 99% (hummer method) single layer		$200/g			
CNFs96%	190–590 nm	€14/g	$16	www.nanografi.com [74]	support by European Union
GO 99.8% 2-5layer		€68/g	$80		
Single layer GO 99.5%		€165/g	$194		
GO99.5%, single layer water dispersion		€38/30 ml	$45		
GNP 99.9% thickness 3 nm and 5 nm		€6-€11/g	$7–13		
reduced GO 2–5 layer		€48/g	$56		
MWCNTs 95%	30–50 nm	€33/g	$39		
MWCNTs 96%	4–16 nm	€33/g	$39		
MWCNTs 96%	8–18 nm	€29/g	$34		
MWCNTs 96%	< 8	€19/g	$22		
COOH&OH Functionalized MWCNTs 96%	4–16 nm	€55/g	$65		
MWCNTs > 95%	< 7nm	$39/g		www.us-nano.com [75]	USA
COOH Functionalized MWCNTs > 95%	< 7nm	$55/g			
OH Functionalized MWCNTs > 95%	< 7nm	$55/g			
MWCNTs > 95%	5–15 nm	$39/g			
COOH Functionalized MWCNTs > 95	5–15 nm	$45/g			
OH Functionalized MWCNTs > 95%	5–15 nm	$65/g			
MWCNTs > 95%	10–20 nm	$39/g			
COOH Functionalized MWCNTs > 95%	10–20 nm	$45/g			
OH Functionalized MWCNTs > 95%	10–20 nm	$45/g			
MWCNTs > 95%	20–30 nm	$29/g			
COOH Functionalized MWCNTs > 95	20–30 nm	$49/g			
OH Functionalized MWCNTs > 95%	20–30 nm	$49/g			
GNP Water Dispersion (99.5%, 6 wt% Average 3–6 Layers		$85/30 ml			
GNP Water Dispersion (95%, 6 wt%, Average 3–6 Layers)		$35/30 ml			
Single Layer Graphene Oxide Nano powder 99.3%		$195/g			
MWCNTs > 95%	8 nm	£60/g	$70	www.ossila.com [73]	UK
MWCNTs > 95%	15 nm	£60/g	$70		
MWCNTs > 99%	8 nm	£90/g	$106		
MWCNTs > 99%	15 nm	£90/g	$106		
COOH & OH Functionalised MWCNTs	8 nm	£120/g	$141		
COOH & OH Functionalised MWCNTs	15 nm	£120/g	$141		
COOH Functionalized MWCNTs > 95	9.5 nm	£74/g	$87	www.nanocyl.com [76]	Belgium

worse[70]. This research indicates that similar phenomena could also occur at the nanoscale.

An overview of Table 3 and Table 4 reveals an important conclusion that almost all researchers have used chemical treatment to dissolve nanomaterials in cement composite along with sonication at the same time. Some chemical treatments can have a positive effect on the dispersion of nanomaterials, but some have had a negative effect like calcium naphthalene sulfonate. On the other hand, in the case of sonication, all researchers have the same opinion on its positive effects. But the frequency of sonication is also an important factor in the better dispersion of nanomaterials. The variable percentage of nanomaterials also affects the effectiveness of dispersion. To understand the importance of using solvents, we can use a comparison between the two researchers'finding. Zhao et al used a solvent (superplasticiser) and Li et al did not have any superplasticiser. While both used almost the same percentage of GO, but when a superplasticiser was used, a positive effect was seen, but without a superplasticiser, a negative effect was seen, which indicates that the GO did not disperse well [45,46]. From the literature, it is clear that the use of the right superplasticiser can enhance the dispersion and thus mechanical properties.

7. Cost analysis and appraisal

There are different price ranges for nanomaterials. Table 5 shows four suppliers from Europe and the USA. One main important influence that can change the price of nanomaterials is the method of production and modification. For instance, when GNP is functionalized by carboxyl (COOH) the price doubles from £15 per gramme to £30 per gramme [71]. The use of functional groups, either hydroxyl (–OH) or carboxyl (–COOH), with nanomaterials can improve their dispersibility in numerous solvents[72]. Another factor that can affect the increasing cost of nanomaterials is purity. If the purity increases the price goes up significantly. For example, a UK supplier sells MWCNTs at 95% purity for £60 and the price goes up when the purity increases to 99% [73]. One factor that can impact the price of GO is the number of layers that GO has. Table 5 shows a single layer of GO is more expensive than GO with 2 to 5 layers and the range of price for a single layer of GO is from €165 to €200 [71,74]. From Table 5 it can be concluded that the diameter cannot make a huge difference in increasing or decreasing the cost of nanomaterials. For instance, MWCNTs with 8 nm are $15 per gramme and MWCNTs with 20 nm is $15 per gramme [71]. The length of nanomaterials also does not have much effect on their price. For example, MWCNTs with lengths from 7 nm to 20 nm have the same price of $39 per gramme[75]. A comparison between CNTs and GO prices shows that CNTs are far cheaper than GO or rGO. In Table 5, the cheapest price of CNTs is $10 per gramme for MWCNTs and the highest price of it is £120 per gramme of functionalized MWCNTs. However, the cheapest price for GO with multi-layers is €68 per gramme and the highest price of it is £200 per gramme. The cheapest product that can be found in Table 5 is GNP from with €6 per gramme[74]. All costs are correct from September 2020 and have been converted to $ at the concurrent market rate for comparative purposes in Table 5.

8. Recommendations leading from critical appraisal

From the studies conducted in the previous sections, it can be concluded that the use of GO leads to achieving better mechanical properties compared to CNTs. It is easier to disperse GO in cement composites because cement particles attach to the edges of GO sheets, and as research has shown, it increases the performance of cement composite better than CNTs. Although the overall price of MWCNTs is cheaper, a review of the literature has shown that less GO material is needed for similar mechanical improvement when compared to MWCNT. This infers a lower total cost for GO when producing, say, 1 m^3 of concrete. On this basis, a cost per required weight would seem a sensible ratio to quantify

Cost per required-weight ratio

$$\mathrm{GO} = /\mathrm{wt}\% = 115 \tag{1}$$

$$\mathrm{MWCNT} = /\mathrm{wt}\% = 43 \tag{2}$$

The ratios (Equation (1) and Equation (2)) show the average price of GO is almost two and half times more expensive than the price of MWCNTs. The average percentage of GO that has been used from Table 1 is about 0.014 wt% and from this table, the average percentage of MWCNTs that has been used is about 0.08 wt% which is five times and a half more than the percentage of GO that is shows GO with small percentage can have better improvement in cement composites compared with MWCNTs.

9. Conclusion

Initial reference guide for researchers and industrialists for adopting nanomaterials in cementitious composites.

This article examines how nanomaterials disperse in water and cement including their effect on the mechanical properties of cement composites. Firstly, the nanomaterials were classified and each of its structures was individually examined. Researchers' analyses on the performance of nanomaterials in cement composites were collected and their findings were then compared.

Secondly, the dispersion within cementitious composites, an important problem of nanomaterials, was addressed. Dispersion has a strong influence on its performance in cementitious composites. The measurement of nanomaterials dispersion and their prices in the last step were discussed.

Some main key points have been concluded from this article

- Dispersion of nanomaterials plays an important role on strength of cement composites and poor dispersion reduce the mechanical properties of cement.
- One of the best SP is AVDA210 and one of the most popular ultrasonic processors is VCX500/750 W.
- There are several ways to measure and analyzed the dispersion of nanomaterials, SEM and UV–Vis, for instance, are appropriate methods to measure good dispersion.
- Adding GO to the cement composite resulted in better improvements in the mechanical properties of cement composites in comparison with other nanomaterials.

- The price of GO is more expensive than CNTs, however, a small percentage of GO is enough to have better improvement in cement composites.

Declaration of Competing Interest

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

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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