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Review

Recent advances in carbon nanotube-geopolymer composite

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HIGHLIGHTS

- State-of-the-art progresses of carbon nanotube-geopolymer composites.
- Dispersion technologies of carbon nanotube in geopolymer.
- Functional characteristics and smart features of resultant composites.
- Mechanisms for property improvement of obtained composites.
- Discussions on current research limits and potential opportunities.

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ABSTRACT

Benefiting from the superior engineering properties and reduced environmental footprints, geopolymer is being considered as an alternative to Portland cement for construction applications. The incorporation of carbon nanotube into geopolymer matrix contributes to improve the mechanical and electrical behaviours of resultant composites. Moreover, the obtained carbon nanotube-geopolymer composite possesses functionalities needed for future, i.e. improved safety and sustainability composed with smart features like self-condition monitoring. This kind of innovative and promising composite is attracting increasing attention from scientific and engineering fields. This work reviews the state-of-the-art progresses in the fabrication and characterization of carbon nanotube-geopolymer composites, including dispersion technologies of carbon nanotube, functional characteristics and smart features of resultant composites, and corresponding reinforcement mechanisms. Discussions on current research limits and potential opportunities are made to promote the investigation and application of carbon nanotube-geopolymer composite as advanced structural material.

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1. Introduction

Geopolymer is an innovative and promising material being considered as an alternative to ordinary Portland cement (OPC) for construction applications. The advantage of geopolymer over OPC includes high mechanical strength at early and final ages, stability under thermal and chemical conditions, strong adhesion to various surfaces, low permeability, low cost, etc. [1–3]. In addition, the CO_2 saving capacity of geopolymer in comparison with OPC was reported up to 90% [4–7]. Under decades of investigation, successes have been achieved in field application of geopolymer constructs, for example, the 4 story high building in Queensland and the Brisbane West Wellcamp airport (BWWA) [8,9]. The former was based on precast geopolymer panels, and the latter was in-situ constructed using 70,000 tonnes of geopolymer concrete. It should be also pointed out that geopolymer tends to be brittle, with the fracture energy about 40% of OPC [10]. Therefore, effects are deemed necessary to improve the fracture performance of geopolmyer. The addition of fibers including steel, basalt, polypropylene, etc., has been demonstrated to be effective in improving flexural strength and fracture energy of resultant geopolymers [11–14]. Apart from these macro-fibres, nanomaterials (such as carbon nanotube (CNT), graphene and its derivatives) are innovative reinforcements due to their superior mechanical, electrical, thermal and chemical properties [15]. Moreover, nanomaterial reinforced OPC/geopolymer composites are endowed with smart features like self-sensing property [16–21].

Civil structures may suffer from deterioration or damage after long-term service or natural disasters. Monitoring and assessing the structural health condition are essential for safety and durability concerns [22]. Conventionally, the structural health monitoring (SHM) was related with devices such as optic sensor, strain gauge, shape memory alloy, etc. [22–27]. The high cost, limited durability, and incompatibility with host structure are technological limits [22]. Meanwhile, the improved safety and smart features of composites developed from nanomaterials reinforced OPC/geopolymer possess the functionalities needed for future infrastructures [20].

To date, nanomaterials reinforced OPC/geopolymer composites have attracted increasing attention from science and engineering fields. In [16–20], the recent progresses in fabrication, state-of-the-art characterization technologies, field applications and challenges of nanomaterial reinforced OPC composites are well reviewed. These works not only offer integrated overview of current state of knowledge, but also critically point out the existing gaps and provide conceptual/practical frameworks for further research. Xie and Fang [28], and Sumesh et al. [29] individually reviewed the incorporation of nanomaterials in geopolymers. However, most attention was paid to the influence of nano-SiO_2, nano-Al_2O_3, nano-TiO_2, nano-Fe_2O_3, nano-clay on the mechanical properties of resultant composites. The performance and mechanism related to smart features are not included. In this work, the fabrication of CNT-geopolymer composites (CGCs) is outlined, various dispersion technologies of CNT are compared and evaluated, conventional properties and smart features of CGCs are addressed, as well as the mechanisms responsible for performance enhancement. Special attention is paid to current research limits and future research directions to optimise the fabrication procedure and to promote its application as advanced structural material.

2. Carbon nanotube

CNT, first discovered in 1991, has been extensively investigated due to its unprecedented properties. Fully comprised of carbon, the microstructure of pure CNT can be visualized as a seamless cylinder rolled from a single sheet of graphite [30]. CNT is normally divided into two subsets: single walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). The latter consists of a set of concentrically formed SWCNT and is consequentially larger than the former [31]. Arc discharge, chemical vapor deposition (CVD) and laser ablation are the methods mainly used for CNT production [30–32]. These methods share the common feature that supplying carbon sources energy to generate-capable fragments for CNT synthesis [33]. The corresponding energy sources of above methods are electricity, heat and high-intensity light (laser) [34–36]. Obtained CNTs are typically washed or ultrasonicated with dilute acid to remove amorphous carbon, residual catalysts and supporting materials [30].

Besides the single-/multi- wall characters, crystalline organization and chiral vector are other main factors defining the structural properties of CNT [37–39]. Intensity ratio of defective carbon band (I_D) and graphitic carbon band (I_G) determined from Raman spectroscopy is normally used to characterize the crystalline organization of CNT [40]. The I_D/I_G also indicates the proportion of organized and disorganized carbon structures [41]. CNT with low I_D/I_G, from 0.65 for laboratory quality to 2.04 for industrial grade, is of highly graphitized structure [37,42,43]. In contrast, chiral vector identifies the geometric organization of hexagonal carbon atom arrays [44], which is particularly relevant for SWCNT to illustrate whether CNT act as metal or semi-conductor [38].

Owning to the abundant C–C bond by analogy with graphite, CNTs exhibit superlative mechanical properties [31,32]. The mechanical performance of CNT was firstly measured using computational simulations, with the Yong's modulus of 1.5 TPa for SWCNT [45]. Other theoretical investigations also confirmed that the Yong's modulus of CNT was around 1 TPa regardless of CNT type and diameter [46]. An average Yong's modulus of 1.0–1.8 TPa was measured for MWCNT, which was based on the amplitude of intrinsic thermal vibration from Transmission Electron Microscope (TEM) [47]. Wong et al. [48] reported a similar result via applying atomic force microscope (AFM) to directly measure the stiffness contact of MWCNT. The mechanical performance of SWCNT locates in similar range, i.e. the Yong's modulus and strength are about 1 TPa and tens of GPa, respectively [49].

In addition, CNTs are also characterized with excellent electrical performance [50,51]. The electrical resistivity of MWCNT bundles was reported approximately 10^{-3} Ω·cm, which is temperature dependent [52]. Resistivity of 5.1×10^{-6}–1.2×10^{-4} Ω·cm at ambient temperature was reported for inidicidual MWCNT [53,54]. The excellent electrical behaviour is related to quantum confinement of electrons stemmed from the one dimensional feature of CNT [55]. Under restraint in radial direction, electrons are destined to propagate only along tub axis. In this case, dispersion of electrons inside the tube is negligible [55]. The high current density of CNT, 10^9 A/cm^2, is also responsible for its extremely low electrical resistivity [56,57].

3. Dispersion of CNT for CGC fabrication

Good dispersion is one of the main prerequisites for the synthesis of CGCs, which also determines the performances of obtained materials [32,42,58,59]. Meanwhile, the agglomeration effect of CNT makes the dispersion problematic. CNT particles tend to remain agglomerated due to the highly attractive van der Waals forces, which is attributed to the high specific surface area characteristic [60,61]. The agglomeration effect is reported to be responsible for the far less than theoretically expected performances of CNT incorporated composites [62–64]. Extensive efforts have been made in the development of effective dispersion technologies, which can be classified into mechanical approaches and chemical treatment [16]. The former includes mechanical agitation, ultrasonication, magnetic stirring, and their combinations, while the later can be further catalogued as covalent and non-covalent treatment [16]. In covalent treatment, aggressive chemicals (H_2SO_4, HNO_3, etc.) are normally used to functionalise the surface of CNT [65–69]. Dispersion based on non-covalent treatment is achieved via the physical attachment between surfactants and CNT surface [32,70]. Though these methods can effectively disperse CNT in aqueous media, each has its disadvantages. For example, the mechanical approaches are normally time-consuming and re-agglomeration of dispersed CNT is often found [71]; covalent treatment may cause structural defects and decline the properties of resultant CNT [72], and non-covalent method suffers from the incompatibility between surfactants and base materials [73]. In practice, a combination of mechanical and chemical approaches is frequently applied for the fabrication of CNT incorporated composites.

Non-covalent treatment together with mechanical agitation or ultrasonication is the most frequently used for the preparation of CGCs, with polycarboxylate-based superplasticizer as a representative surfactant [42,58,74]. The ultrasonication time ranges from tens of minutes to a couple of hours, which depends on the power capacity of ultrasonic processor, concentration of dispersant and CNT dosage [42,58,74].

Heister et al. [77] stated that NaOH solution can remove the oxidation debris from CNT surface and promote its dispersion efficiency. Thus, the alkaline solution used for geopolymer synthesis has the possibility of serving as surfactant and allowing de-agglomeration. Practices in dispersing CNT into alkaline activators were reported in [74,78,79]. According to da Luz et al. [79], well dispersion can be achieved by 30 min ultrasonication. The dispersion efficiency and stability are determined by CNT type and amount, as well as concentration of alkaline activator [74,79]. Re-agglomeration of pristine CNT during geopoymerization was visibly observed whilst the functionalized CNT system not [79]. This is because that the surfaces of CNT become hydrophilic after acid treatment [79]. Saafi et al. [74] concluded that increasing NaOH concentration from 8 mol/l to 12 mol/l improved the dispersion of CNT.

Bi et al. [75] designed a unique chemical treatment method, i.e. coating SiO_2 on CNT, which not only promoted dispersion of CNT in alkaline activator but also improved the interaction between CNT and geopolymer matrix. Raw CNT was firstly treated using the mixed solution of HNO_3 and H_2SO_4, followed by repeated washing with deionized water until the pH value was approximately neutral. After vacuum drying, the acid treated CNT was dispersed into mixed solution of ethanol, deionized water and NH_4OH to get a stable and homogeneous suspension. Tetraethyl orthosilicate was then added for further functionalization. To remove free silica and improve the quality of SiO_2 coated CNT, obtained sediment was dispersed into water, filtrated and dried for several cycles. According, the SiO_2 coated CNT can be effectively and uniformly dispersed into alkaline activator.

Apart from dispersing CNT in aqueous media, preferential mixing of CNT with solid precursors was also reported [59,76]. Mac Kenzie and Bolton [59] directly mixed CNT with geopolymer precursor. Mixture was then mixed with alkaline activator to get CGC slurry, similar with the conventional synthesis procedure of geopolymer. Notably, details about the dry mixing procedure were not given. Though the obtained CGC possess better electrical property than the control samples (CNT-free), the mechanical behaviours vary marginally. All these limit the evaluation of the efficiency of dry mixing and dispersion state. Yuan et al. [76] introduced a modified mixing procedure, in which the CNT was dispersed into sodium dodecyl sulfate solution and then mixed with solid precursor in ethanol. After drying and screening, the mixed powders were further blended with alkaline activator for CGC fabrication. Different from the direct dry mixing in [59], this method facilitates the homogeneous mixing of CNT and solid precursor.

4. Properties of fresh CGC

To data, only limited attention has been paid to the workability of fresh CGC. Decrease in workability, increase in viscosity and yield stress have been observed in CNT-cement system [80–82]. This is assigned to the high specific surface area of CNT. In [79], the mini-slump consistency and yield stress of CGC locate in the similar range as plain geopolymer without CNT addition, and only marginal difference was observed [79]. Similar results were achieved by increasing CNT addition or replacing pristine CNT by acid treated counterpart. The insignificant change in workability might be partially caused by low CNT dosage, as only up to 0.2 wt% CNT was used [79]. Difference in chemistry between cement hydration and geopolymerzation might also be responsible. Cement system is composed of high content of calcium-bearing crystals (alite, belite, aluminate and ferrite) [83]. Ions released from the dissolution of these phases facilitate the formation of calcium silicate hydrates (C-S-H), portlandite and ettringite, some of which are well crystallized [6,83]. In contrast, both solid precursors and main reaction products of geopolymer are X-ray amorphous [84–86]. In [87–89], accelerated hydration process was observed due to the incorporation of CNT. Much higher Vicker's hardness was detected in CNT incorporated cement pastes than control specimen, which disappeared after 14 days. Makar et al. [87] stated that CNT, even in bundled form, serves as nucleating sites for the growth of reaction products. Moreover, CNT was found to alter the hydration morphology [90]. No study about the influence of CNT on geopolymerization has been published, which is worthwhile for future investigation.

5. Properties of hardened CGCs

5.1. Mechanical properties of CGCs

Extensive efforts have made in investigating the influence of CNT on mechanical properties of obtained CGCs. Table 1 gives a short summary of the mechanical enhancement of CNT on CGCs Generally, an addition of very small amount of CNT leads to significant mechanical enhancement. For example, Abbasi et al. [58] reported that the flexural strength and Young's modulus of fly ash based CGC incorporating 0.5 wt% MWCNT was correspondingly 128% and 109% higher than plain geopolymer. Mechanical properties of CGCs are well related with the dispersion effect of CNT in

Table 1
Short summary of the improvement of CNT on mechanical behaviours of CGCs.

Matrix	CNT type	CNT content	Dispersion method	Mechanical improvement	Reference
Metakaolin geopolmyer	MWCNT	0–1 wt%	MWCNT was mixed with Plastit SPCA$_{100}$, a polycarboxylate-based superplasticizer, and then ultrasonicated in water bath at 20 °C for 20 min.	CNT addition in the range of 0–1 wt% contributed to increase both compressive and flexural strength of obtained CGC. The highest mechanical improvement was achieved by CNT addition of 0.5 wt%, with the compressive and flexural strength increase of 32% and 66%, respectively.	[58]
Fly ash geopolymer	MWCNT	0–0.2 wt%	MWCNT was initially mixed with carboxymethyl cellusose. Mixture was dissolved in hot water and mechanical homogenized at 14000 rpm for 3 h.	Compressive strength enhancement by 30%, 50%, 70% and 17% was achieved by adding 0.05%, 0.1%, 0.15% and 0.2% CNT. Reduction in fracture toughness was observed at CNT dosage up to 0.1%, followed by slight increase with higher CNT addition.	[92]
Fly ash geopolymer	MWCNT	0–5 wt%	CNT was mixed with NaOHsolutions of 5, 10, and 15 M concentrations.	CNT addition at 1–2% leads to increase of compressive strength, whilst, higher CNT dosage results in strength decrease compared with plain geopolmyer. The highest strength increase (32%) was observed at CNT addition of 1 wt%.	[78]
Clay geopolymer	SWCNT	0 – 0.3 wt%	CNT was directly mixed with solid precursor.	Tensile strength of potassium silicate activated CGC stay in similar range, while strength of sodium silicate activated CGC varies significantly. In general, the tensile strength of resultant CGC is not considerably improved.	[59]
Fly ash geopolymer	MWCNT	0–1 wt%	Solution containing 5% Glenium 51 polycarboxylate-based superplasticizer and 95% water was used as surfactant. CNT was mixed with surfactant and then ultrasonicated for 2 h.	The flexural strength, flexural toughness and Young's modulus increase with the addition of CNT up to 0.5 wt% and then drop to close to plain geopolymer at CNT addition of 1 wt%. The enhancement of flexural strength, flexural toughness and Young's modulus at 0.5 wt% CNT content is 128%, 207% and 109%, respectively.	[74]
Metakaolin geopolmyer	MWCNT	0.1 wt%, 0.2 wt%	CNT was mixed with alkali activator and sonicated for 30 min.	The addition of 0.1 wt% CNT improved the compressive and flexural strength of CGC by 13.2% and 28.7%, respectively. Meanwhile, compressive and flexural strength decrease by 11.8% and 31% was observed by adding 0.2 wt% CNT. CNT addition showed marginally influence on dynamic Young's modulus.	[79]

geopolymer matrix as well as the interaction between both materials [58,79]. When surpassing a certain amount, CNT addition would result in strength loss. High CNT loading amount considerably raise the difficulty in uniformly dispersing CNT in geopolymer matrix. Agglomeration of CNT is reported to be responsible for the decline of CGCs with high CNT addition [58,79]. Agglomeration not only decrease bonding between geopolymer and CNT but also increased the porosity [78]. Both are negative for mechanical performance of resultant CGC. The percolation threshold is determined by initial property of CNT and mix design of geopolymer binder. A threshold of 0.5 wt% and 0.1 wt% was reported in for fly ash geopolymer and metakaolin geopolymer, respectively [74,79]. Compared with pristine CNT, no threshold was observed for functionalized CNT within the same dosage range [79]. This is constant with the cementitious system that chemical treatment is deemed to be most successful in improving the mechanical properties of resultant composites [67–69,91]. After treatment, the functional groups on CNT surfaces chemically interact with hydration/geopolymerization products and consequently increase the bond strength between CNT and matrix [32,79].

In [59], the tensile strengths of CGC specimen incorporating different contents of CNT are similar with (in some cases lower than) the control mix. This might be caused by the inhomogeneous distribution of CNT into geopolymer matrix, which stemmed from the pre-mix of CNT with solid precursor. Moreover, the aggressive mechanical pre-mix might cause damage to CNT and increase defects, which weakens the positive contribution of CNT. Pre-mix of geopolymer precursor with CNT was reported in [76], in which a wet mixing procedure was applied. Though a percolation threshold was observed in terms of the evolution of flexural strength, elastic modulus and fracture toughness, the threshold value (3 wt%) is much higher than other studies [74,78,79].

The significant improvement of CNT on mechanical behaviors of CGCs was firstly assigned to the physical nano-filler effect. As aforementioned, the excellent mechanical behaviors of CNT make it suitable as reinforcing filler on organic, metallic and cementitious materials [31,62,93]. A characterization of porosity shows that addition of CNT below the threshold leads to the decrease of total porosity and macro pores, contributing to the strength incensement of resultant CGCs [78,79].

Enhancement in load transfer between CNT and geopolymer matrix as well as the crack-bridging property of CNT are beneficial for the mechanical improvement of CGCs [74,79]. The shear-lag model, shown as equations (1) – (3), was often used to describe the load transfer of nanotube reinforced composites [94].

$$\sigma_f = E_f \varepsilon \left[1 - \frac{\sinh\left(\frac{2\lambda\alpha x}{l}\right)}{\cosh(\lambda\alpha)} \right] \tag{1}$$

$$\tau_f = \frac{\lambda E_f \varepsilon}{2} \left[\frac{\sinh\left(\frac{2\lambda\alpha x}{l}\right)}{\cosh(\lambda\alpha)} \right] \tag{2}$$

$$\lambda = \left[\frac{4G_m}{E_f \ln\varphi_f} \right]^{\frac{1}{2}} \tag{3}$$

where

σ_f the tensile stress of CNT (Pa),
τ_f interfacial shear stress along CNT length (m),
E_f modulus of CNT (dimensionless),
ε strain of CNT (Pa),
α aspect ratio of CNT (dimensionless),
G_m shear modulus of geopolymer matrix (dimensionless),
φ_f volume fraction of CNT (dimensionless).

It can be inferred from above equations that the high aspect ratio and modulus property of CNT promote load transfer from geopolymer matrix to CNT. As a consequence, strength and stiffness can be considerably improved when the CNT is adequately dispersed. The interfacial stress helps to enhance the fracture toughness. This is supported by the much higher fracture energy of CGC than plain geopolymer [74,95].

Above findings are based on the characterization of CGCs at ambient temperature. Meanwhile, the mismatch of thermal expansion coefficient between CNT and geopolymer matrix may damage the integrity of CGCs. Formation of large numbers of cracks after thermal treatment has been observed in CNT reinforced composites [96–98]. Effect of thermal treatment on flexural strength, elastic modulus, flexural toughness of CGC was investigated in [76]. Treatment at 950 °C improved the elastic modulus by 2 times and enhanced the fracture toughness by 6 times. The mechanical behaviors increase with the increase of temperature up to 1100 °C, followed with a little variation at even higher temperatures [76]. No crack induced by the mismatch of thermal expansion coefficient was observed under SEM characterization. This can be assigned to the low content of CNT and its well dispersion state [76]. The shrinkage of CGC under thermal treatment can be divided into four stages (Fig. 1) [76]: stage I from ambient to about 100 °C showed minimal shrinkage due to the loss of free water from surface and large pores; stage II locates in the temperature range of 100 °C – 300 °C, which is assigned to capillary contraction induced by water evaporation form micro and nano pores; stage III, from 300 °C to 800 °C, is caused by the physical contraction of geopolymer matrix at high temperatures, including the condensation conversation of T-OH groups to T-O-T linages [99]; further increasing temperature, the framework densification and pore elimination by viscous sintering are responsible for the significant shrinkage at stage IV, which accounts for over 60% of the total shrinkage. And benefiting from the viscous sintering process, the microstructures of CGC become more compact after thermal treatment, which contributes to the improvement in mechanical behaviors as abovementioned.

5.2. Electrical properties of CGC

Hanjitsuwan et al. [100] stated that the electrical conductivity of plain fly ash geopolymer ranges from 10^{-5} S/cm to 10^{-2} S/cm. An average value of 0.77 S/m was reported in [101], which is in well agreement with the results from [100]. Notably, the electrical conductivity of geopolymer is influenced by mixture formulation, curing condition and measurement methods. Reactivity of solid precursor and liquid-to-solid ratio determines the development of pore structure and composition [102]. A decrease of porosity can result in the reduction of ion conductivity of plain geopolymer, which consequently increases the internal resistance and decreases the capacitance [100,101].

Increase of electivity conductivity with the increase of frequency in 100 Hz-10 MHz was observed in [100], whereas, a threshold frequency of 25 Hz was detected in [101]. A close check of these studies shows that conductivity measurement was operated using different methods, i.e. geopolymer pastes were coated with silver in [100], while four copper electrodes were embedded during specimen preparation in [101]. The differences in measurement technologies limit the comparison of above individual studies for a conclusive decision. Further studies are thereby required.

Dramatic improvement of electrical property of geopolmyer can be achieved by adding a small amount of CNT [74,103]. Fig. 2 depicts the impedance change of CGC with different CNT dosages. In general, the impedance decrease with the increase of CNT content as well as the increase of frequency. The enhancement can be attributed to the improvement in conductive network with the presence of CNT [74]. At low incorporation content, CNTs are separated by thin geopolymer layers. The tunnelling gap controls the electron flow and affects the overall conductivity. Increasing CNT dosage can consequently improve the formation of conductive path, and somehow allows the formation of multiple paths through surface contacts [74,103]. Different from the negative effects of CNT agglomeration on mechanical properties, the agglomerated bundles can be regarded as 'conductive islands' helping the formation of percolation networks within the matrix [74,75]. Similar phenomena have been observed in different CNT incorporated composites [104–106].

The incongruent changes of electrical and mechanical properties caused by CNT addition should be taken into consideration for the fabrication of CGCs, especially those designed for structural application. Possible ways to achieve a balance between decrease in mechanical behaviours and increase of electrical performances deserves further investigation.

5.3. Durability of CGC

Durability of a construction material determines its commercialization and field application potential. The water adsorption capacity can partly represent the transport property of investigated materials. Generally, the more permeable a material, the high potential the aggressive medias penetrate and damages generate [16]. Addition of CNT below percolation values noticeably reduces the water absorption. The improved reaction process and decreased porosity are responsible [42]. In addition, the initial hydrophobic property of CNT might also be related. The graduate increase of water adsorption with CNT addition over percolation content is assigned to the agglomeration effect [42].

The drying shrinkage represents to some degree the plasticity of a material. And most of the drying shrinkage of cementitious material occurs at early ages. The high shrinkage of the control mix can be assigned to low reaction extend or formation of zeolite structures [42]. The zeolite phases are generally high-water content and can increase the shrinkage of cementitious materials [107,108]. CNT dosage leads to the formation of more compact structure, which contributes to decrease the shrinkage values of CGCs. Meanwhile, hardly fully avoided agglomeration and bundling of CNT at high adding content is responsible for the gradual shrinkage increase. It should be pointed out that there's obviously wide gap in terms of shrinkage value between plain geopolymer and CGCs [42].

5.4. Microstructure of CGC

The macro-properties, including mechanical and electrical properties as well as durability, are closely related with the microstructure. Fig. 3 shows the typical morphology of fly ash and metakaolin based CGCs. Good dispersion can be directly seen from Fig. 3(a–c), in which the additions of CNT are under the corresponding threshold values. Individual CNT distributes throughout the matrix with a uniform density. In addition to filling pores and voids, the CNTs are involved in bridging hollow spaces and

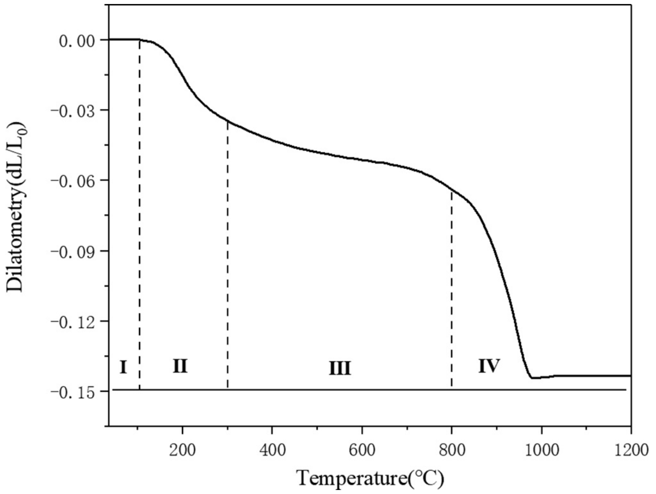

Fig. 1. Thermal shrinkage curves of CGC (metakaolin geopolymer activated by potassium silicate solution, CNT content 3 wt% by mass of metakaolin) [76].

micro cracks [58]. The crack-bridging effect of CNT contributes to decelerate the initiation and extension of cracks [58,74,75]. Mechanical properties of CNT are estimated much better than geopolymer. The propagation, delfection and branching of micro cracks mush pass the nanotubes or take place in areas where week interactions between matrix and CNT [21]. Bond state is then essential in determining the macro properties of CGCs. A well bond can be inferred from the microstructure without obvious interfacial layer between CNT and geopolymer matrix, which also indicates the chemical stability of CNT under geopolymerization. A schematic illustration of the interface between SiO_2 coated CNT and geopolymer matrix is shown in Fig. 4. Under chemical attack of alkaline activator, the amorphous phases from solid precursors and the amorphous SiO_2 coated on the surface of CNT can be easily dissolved and take part in geopolymerization. The SiO_2 coated CNT then not only favors the reaction but also contributes to form strong interfacial interactions [75].

In contrast, when large amount of CNT was incorporated, agglomeration is practically inevitable. The loss or evaporation of water adsorbed by agglomerated CNT bundles increases porosity of obtained CGC [78,79]. As reported, increase of total porosity by 19% was detected when CNT addition is beyond the threshold value [79].

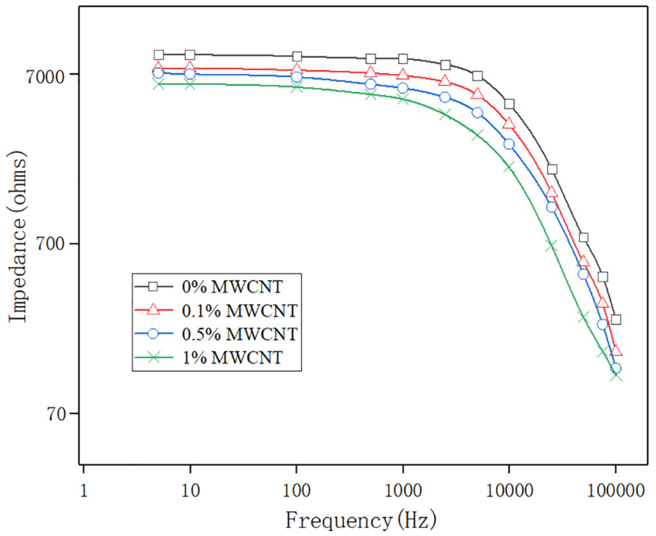

Fig. 2. Impedance of CGC (fly ash geopolymer activated by NaOH solution of 12 mol/l). adapted from [74].

No influence of CNT on reaction products of CGCs has been observed via X-ray diffraction (XRD), Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectrometer (FTIR) methods, even though that CNT can act as nucleation sites and accelerate geopolymerization [42,58,76,79]. This can be caused by the dosage of CNT is in very small amount which cannot be effectively detected by above methods. The high amorphous characteristic of geopolymer and the coexisting of geopolymeric gel and partially reacted or unreacted precursors hinders a deep and quantitative analysis. More advanced technologies are then required for further investigation.

6. Smart features of CGC

The piezoresistive effect of a sensor is classified as the ability to monitor the change of electrical resistance induced by external mechanical strain and to evaluate the stain by assessing resistance change [109,110]. In [111], the piezoresistivity of plain geopolymer paste was first characterized. Briefly, geopolymer pastes behave like a pure capacitor at frequency 0.1 Hz – 1 Hz, due to the highly capacitive property. At frequency higher than 1 Hz, the real impedance of geopolymer paste roughly equals the bulk resistance, and the imaginary impedance is very negligible. Based on this, geopolymer pastes can be considered as pizeoresistive stress sensor. Decrease of impedance with the increase of load was also observed [111]. The calculated sensitivity was 11 Ω/MPa after applying a linear fit between the impedance change and applied load. Fig. 5 presents a schematic illustration. The corresponding mechanism is hypothesized that the lattice structure of geopolymer changes in a way that the jumping distance of alkali metal ions within geopolymer matrix through the inter-connected diffusion channels is shortened under applied compressive load [111]. The decrease of hopping distance leads to enhanced hopping conductivity [112]. In bending or flexural tests, this is represented vice versa, i.e., an increase in hopping distance and electrical resistance.

CNT possesses significant influence on pieroresistive effect of obtained CGCs [74,75]. The load–deflection responses of CGC beams (100 mm × 100 mm × 500 mm, equipped with 4 copper electrodes) are shown in Fig. 6, from which a nearly linear load–deflection behaviour up to failure can be seen. The addition of CNT, especially at content 0.1 wt% and 0.5 wt%, improved the stiffness, ductility and load carrying capacity of CGC. Due to the stress concentration induced by agglomeration effect, the one with 1 wt% CNT dosage showed similar load-deflection behaviour with plain geopolymer specimen. In Fig. 6(b), the impedance changes linearly to the change of deflection below failure load. Under bending test, the electrical resistance of CGC is increased because the applied stress increases the distance among geopolymer binder, CNT and ion-containing pores [74]. With the increase of tensile stress, the degradation of existing conductive paths becomes more considerable, which leads to the gradually increase of electrical impedance. Crack initiation can be inferred from the sudden increase in impedance and the sudden drop in applied load during test. Further progression of cracks generates successive open-circuiting within CGC samples. At failure load point, the lacking of complete conductive path results in abrupt increase of impedance.

Bi et al. [75] quantitatively analysed the self-sensing property of CGC. The gauge factor (GF), representing the piezoresistive response of studied materials, is defined as the ratio of relative change in electrical resistance to mechanical strain (Eq. (4)).

$$GF = \frac{\Delta R/R_0}{\varepsilon} \tag{4}$$

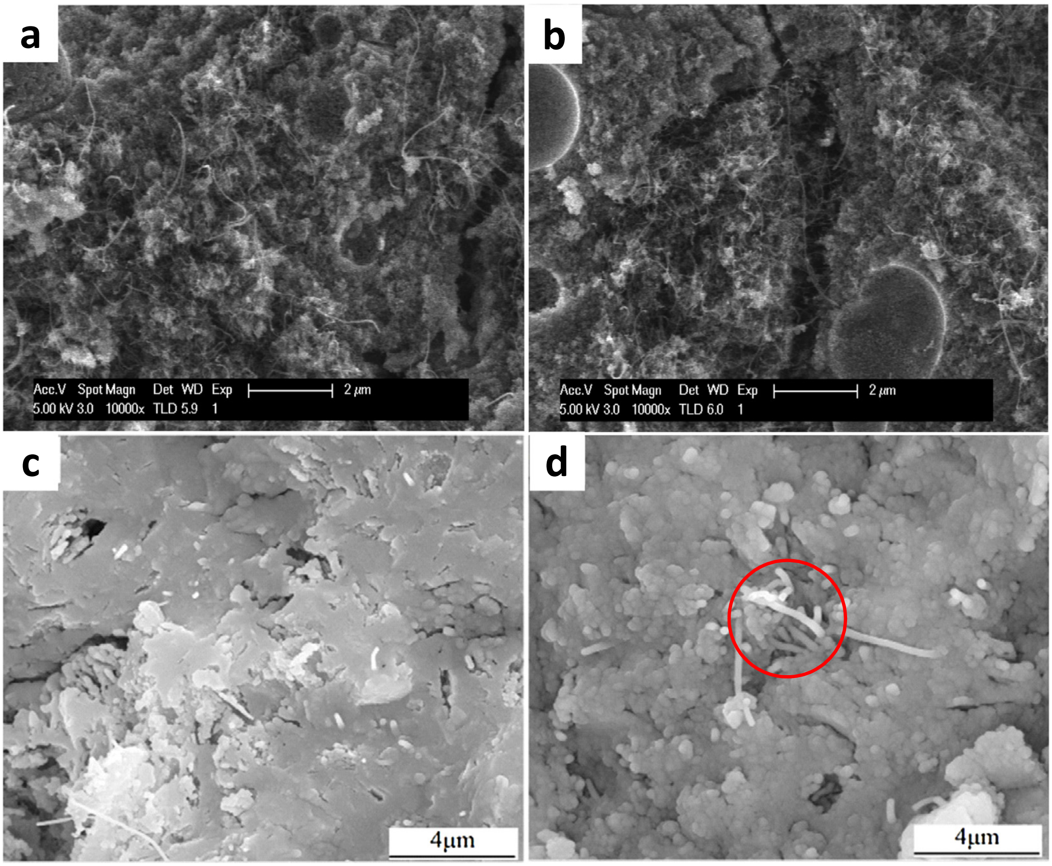

Fig. 3. Microstructure of CGC (a and b: fly ash geopolymer with 0.1 wt% CNT and 0.5 wt% CNT (percolation value 0.5 wt%) [74]; c and d: metakaolin geopolymer with 3 wt% CNT and 5 wt% CNT (percolation value 3 wt%) [76]).

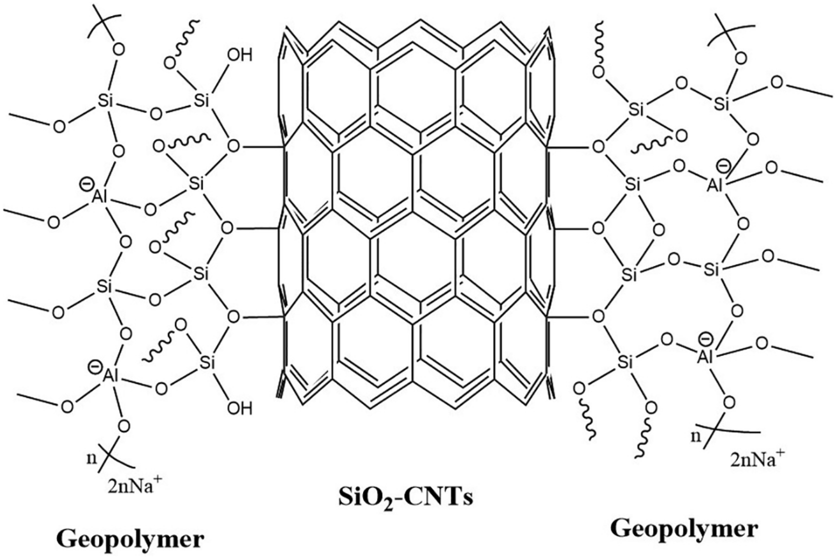

Fig. 4. Schematic illustration of the interface between SiO_2 coated CNT and geopolymer matrix [75].

where

R_0 initial electrical resistance
ΔR change in electrical resistance
ε applied strain.

Similar with the results shown in [74], $\Delta R/R_0$ continuously increased with the increase of applied stress until an abrupt increase (in flexural tests) or drop (in compressive tests) was detected. GF significantly increased after adding 0.25 wt% CNT. The improvement was assigned to the enhanced conductive paths after adding CNT [74,75]. The enhancement in electronic conduction is determined by factors including the intrinsic resistance of CNT and the contact resistance at the joints. The former is expected to be negligible because the excellent electrical conductive property of CNT [32], whereas, the latter depends on the CNT type. Compared with pristine CNT reinforced CGC, the one incorporated with SiO_2 coated CNT benefits from restoration of intrinsic conductive property of CNT, better dispersion effect and more effective connections [75]. All these contribute to more pronounced improvement in self-sensing sensitivity. The gauge factor are much higher than recently reported cementitious materials incorporated with CNT, carbon blacks, carbon fibres, graphene and its derivatives (listed in Table 2) [75,101,113–116]. The unique behaviours of CGC indicate the potential application as self-sensing materials for SHM.

7. Further research perspectives

Recent investigations on CGCs mainly focus on the fabrication methods, enhancement in mechanical and electrical properties, and piezoresitive effect of obtained composites. Though results are promising and shape a great future, practices involved are scant and scattered. More efforts are deemed necessary to bridge the gaps in CGC design, fabrication/processing, characterization, simulation and modelling.

The general design principle is to tailor CGC based on specific application demands integrating the genetic characteristics of nano science and technology [20]. Approaches including bottom-up, top-down and their combination can be adopted in CGC design, in which the effectivity, economy and sustainability should be taken into consideration. Moreover, a combination of computational tools and experimental techniques is supposed to accelerate the design process, given that the experimental variables involved are too many and the relationships among them are too complex [117,118].

The key issue for CGC fabrication is the uniform dispersion of CNT. Currently, most attention is paid to dispersion techniques, with few publications focusing on the dispersion state. An effective evaluation of dispersion state can be achieved by image analysis and resistivity measurement [16,32]. Image analysis is based on the morphology characterization using SEM, AFM or optical microscope, from which dispersion state and agglomeration of CNT can be qualitatively evaluated. In resistivity measurement, it is hypothesized that uniform dispersion of CNT results in low resistivity because the well formation of electrical conductive pathways [119]. It should also be mentioned that both methods based on the characterization of hardened CGC specimens, which is time and effort consuming. Repaid evaluation, for example directly evaluating CNT containing aqueous media based on spectroscopy, is expected.

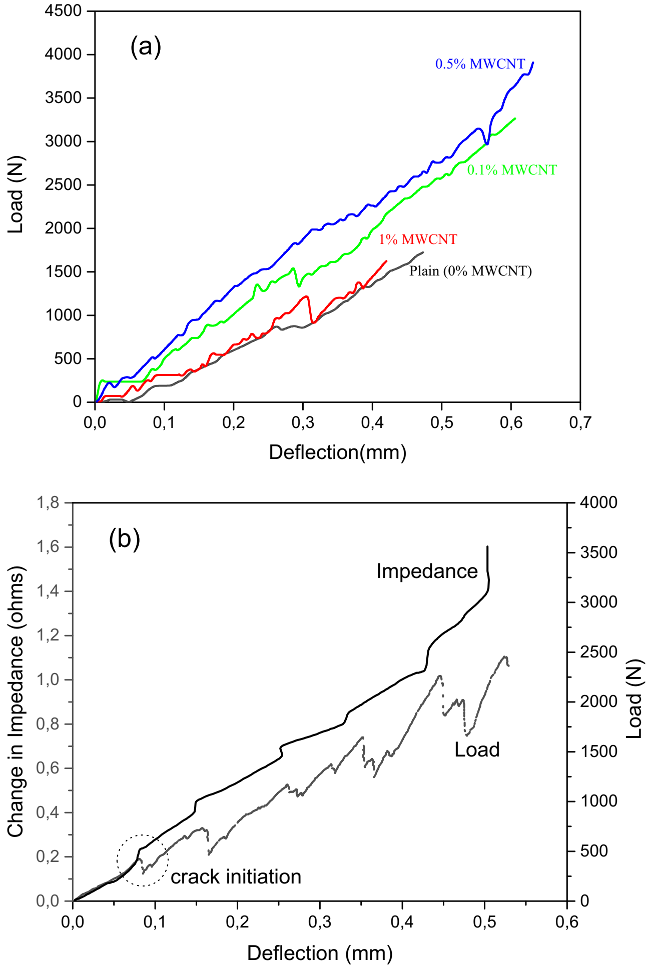

Fig. 6. Load-deflection response (a) and impedance-deflection response (b) of CGC (adapted from [74]).

In many publications [58,74,79], acceleration effect of CNT on geopolymerization has been stated, whilst direct robust characterization on geopolymerization degree is mising. Apart from (semi-) quantitive analysis on reaction kinetics, whether CNT can selectively affect the distribution of dissolved ions deserves detailed investigation. SEM coupled with Energy-dispersive X-ray

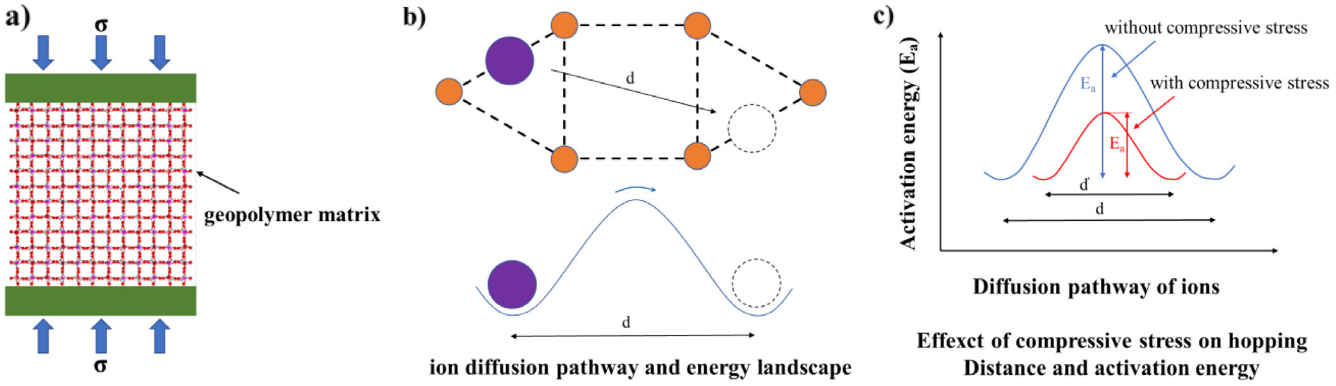

Fig. 5. Schematic illustration of self-sensing mechanism of geopolymer paste, (a) geopolymer paste under stress, (b) pathway and corresponding energy landscape of ion diffusion, (c) influence of stress. adapted from [111].

Table 2
Gauge factor of cementitious composites under compression test.

Composite	Gauge factor	Reference
Metakaolin geopolymer + 0.26 wt% SiO_2 coated CNT	663.3	[75]
Fly ash geopolymer + 0.35 wt% reduced graphene oxide	43.9	[101]
Cement + 1 wt% MWCNT	130	[113]
Cement + 1 wt% carbon fibre	332	[114]
Cement + 15 wt% carbon black	55.3	[115]
Cement + 0.5 wt% carbon black + 0.5 wt% carbon fibre	17.3	[116]

spectroscopy (EDS) is powerful for this kind of characterization. In addition, the interaction or bonding between CNT and geopolymer matrix can be characterized based on SEM. When AFM is applied, pull-out and peeling experiments can be conducted for interaction investigation [120–123]. Besides experimental techniques, modelling methods, such as molecular dynamics, coarse grain simulation and density functional theory, are recommended. Take the molecular dynamics for example, which is powerful in simulating nanoscale systems using the physics of particles and the motion principles [124]. With this method, parameters determining the interactions of various CNT reinforced composites have been reported [125–127].

The interfacial stress transfer is one of the main system requirements for effective reinforcement [31]. It is expected that the external stress applied to CGC could be effectively transferred to CNT for disproportionate share of the load [31]. Studies have demonstrated that the interfacial stress shear strength governs the stress transfer to CNT [31,128]. Though practices have been reported in measuring interfacial shear strength of CNT incorporated composites using TEM or AFM, it is still very challenging [122,129–131]. Computational work seems to be more practical, and successes have been achieved in predicting the interfacial shear strength for fibre reinforced composites [132–136].

8. Conclusion

The present work provides state-of-the-art information on the fabrication and properties of CGCs. The most frequently used dispersion technology is a combination of non-covalent treatment and mechanical agitation or ultrasonication. And polycarboxylate-based superplasticizer is a representative surfactant. In addition, alkaline activator for geopolymer synthesis can act as de-agglomeration media. Chemical treatment of CNT helps improve the dispersion efficiency. Mechanical mixing CNT with solid precursor is included in this work but not recommended due to that aggressive mechanical pre-mix can cause damage to CNT and increase defects. Both the mechanical and electrical properties of obtained CGCs depend on the quality and content of CNT. A percolation threshold is observed in terms of the reinforcement on mechanical properties rather than electrical behaviours, which is related to the initial property of CNT and mix-design of geopolymer. CNT can significantly enhance the pieroresistive effect of obtained CGCs. The unique behaviours of CGCs, comparable or even higher gauge factor than CNT-cement composites, indicate that CGCs possess the capacity to be used as self-sensing materials for SHM (structural health monitoring). It should also be mentioned that practices currently involved in CGC investigation are still scant and scattered. The promising results shape a great future but require further efforts to bridge the science and engineering gaps in design, fabrication, characterization, simulation, modelling and application of CGCs.

Declaration of Competing Interest

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

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