Chapter 7

Nanomaterials in Structural Engineering

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Abstract

Development of structural engineering, daring structures with record spans or heights, meets two serious obstacles—the limitations of traditionally used materials and the need of continuous monitoring of new structures subjected to complex loads, including those of dynamic nature. Considering the responsibility for the life of people and the budget of new structures, the need of constant monitoring is inevitable. This is why structural engineers seek for new solutions; among them, smart structures based on self-monitoring materials seem to be one of the most attractive proposals. It is still an unexplored area, but current research shows a high potential of the use of composites reinforced by carbon-based nanomaterials as self-sensing structural materials. Nanomaterials also influence other important features of structural materials, such as microstructure, mechanical, and transport-related properties. In this chapter, we present the state of art of the use of nanomaterials in structural engineering in various areas including mechanical and electrical properties as well as issues referring to durability.

Keywords: nanomaterials, structural engineering, graphene, smart materials, smart structures

1. Introduction

In 1959, during the Meeting of the American Physical Society at CalTech, the physicist Richard Feynman gave his famous speech entitled *"There's plenty of room at the bottom,"* and thus, the new nanotechnology era begun [1]. Feynman presented the idea of modifying and controlling matter at the scale of individual atoms and molecules [2]. However, it was only in 1974 when the term *"nanotechnology"* was created by Norio Taniguchi and was defined as processing materials by one atom or by one molecule [1, 3]. Since then, the definition of *"nanotechnology"* has been modified several times over the years. Today, it can be defined as *"the application of scientific knowledge to manipulate, control and restructure matter at the atomic and molecular level in the range of 1–100 nm to exploit the size-dependent and structure-dependent properties and phenomena distinct from those at different scales"* [3]. Basically, nanotechnology is based on the statement that we can change any property of any material with reducing at least one dimension of this material into the nanoscale [4].

While nanotechnology has attracted attention in many fields of science and technology, including chemistry, electronics, medicine, or biology, its application in civil engineering, up to date, remains limited [1, 5–7]. These days, searching in SCOPUS database for the terms *"nanomaterial"* AND *"civil engineering"* within titles, abstracts and keywords of published papers returns only 18 document results. The RILEM TC 197-NCM Report [5] has highlighted, for the first time in 2004, the potential applications of nanotechnology in construction materials. The e-mail survey carried out among researchers, construction professionals, and large construction companies was the basis of reported information. The report revealed that little awareness of nanotechnology applications in construction is an effect of insufficient information on this subject. Therefore, nanotechnology was perceived as expensive and highly complex, thus discouraging potential customers. However, the results of the survey have shown that nearly 100 research projects carried out by respondents were based on nanotechnology. The potential nanotechnology applications were pointed out as follows:

- understanding nanostructure of materials,
- nanostructure modification of materials,
- functional films and coatings,
- smart structures and devices,
- environment-friendly applications [5].

Since then, research introducing nanotechnology in civil engineering has followed mainly these abovementioned development paths.

This chapter presents a review of the achievements of nanotechnology in Structural Engineering with special emphasis on improved physical parameters of structural materials and their potential in strengthening repairs and Structural Health Monitoring.

2. Improvement of mechanical properties and durability

Improvement of mechanical properties and durability of cementitious materials is mostly obtained by their nanostructure modification, that is, the incorporation of nanomaterials into cement matrix. Nanoparticles possess a high chemical reactivity due to a high surface area and can promote the growth of cement hydration products. Nanomaterials employed in cementitious composites, up to date, are nano-silica, nano-titania, nano-iron oxide, nano-alumina, nanoclay particles, carbon nanotubes, graphene oxide (GO), and graphene nanoplatelets (GNPs) [7].

Nano-silica (nano-SiO_2) is proved to enhance the compressive, tensile, and flexural strength of OPC pastes and mortars [8]. The addition of nano-SiO_2 effects in denser cement paste microstructure with improved porosity thus leads to a decreased water penetration and sorptivity [8] and therefore to the reduction of calcium leaching [9]. Nano-alumina (nano-Al_2O_3) matches the performance of nano-silica—it leads to a more compacted microstructure of cementitious composites, decreases their porosity, and enhances the compressive strength [10, 11]. It is worth noting that nano-alumina was proved to improve concrete performance at both elevated and low temperatures [10, 11]. The incorporation of nano-titania (nano-TiO_2) may lead to the enhancement of compressive and flexural strength as well as to the improvement in the resistance to chloride penetration due to a refined pore structure of the composites [12]. The impact of nano-titania addition on the performance of cementitious composites at an elevated temperature turned out to be comparable to composites incorporating nano-alumina [13].

However, the most studied nanomaterials to be used in cementitious composites are carbon-based nanomaterials. Until 1985, only two allotropic forms of solid carbon had been known, these had been diamond and graphite, which both feature covalently bonded networks [14]. In 1985, the new era of carbon nanomaterials had begun, when fullerenes—molecules composed of 60 carbon atoms, C60—had been discovered [14, 15]. It was less than 6 years later when it turned out that carbon atoms can also form cylindrical tubes. In 1991, Iijima [16] observed first the multi-walled carbon nanotubes (MWCNTs) and then in 1993, Iijima and Ichihashi [17] reported single-walled nanotubes (SWCNTs).

CNTs possess extraordinary electrical, thermal, and mechanical properties, highly relying on their dimensions. The diameters are in the range of 1.4–100 and 0.4–3 nm for MWCNTs and SWCNTs, respectively. Young's modulus for SWCNTs and MWCNTs is equal to ca. 1 and 0.21 TPa, respectively, while the tensile strength for both types of CNTs reaches 500 and 10–63 GPa [15].

Manufacturing of cementitious composites incorporating carbon-based nanomaterials is an extremely challenging task due to the crucial problem of obtaining a homogeneous dispersion of a nanomaterial within cement matrix. Carbon-based nanomaterials are prone to form aggregates and bundling as an effect of both their high hydrophobicity and strong van der Waals forces [18–20]. Nonuniformly dispersed nanoparticles strongly influence the workability and microstructure of cement composites and hinder the ongoing hydration; thus, it is of significant importance to adopt an appropriate treatment to obtain a sufficient consistency and dispersion of nanomaterial within cement matrix.

Several different attempts to obtain a homogeneous dispersion of CNTs in cement mix were reported, including carboxylation of CNTs [21], that is, special treatment to attach carboxylic acid to their surface or functionalization of CNTs with COOH groups [22, 23]. Nevertheless, the main approach employed to fabricate cement-CNT composites is, clearly, stirring and ultrasonication of aqueous dispersion of CNTs with various types of surfactants, such as polycarboxylic acid-based superplasticizers [23–25], anionic sodium dodecyl sulfate [20, 26], sodium dodecyl benzene sulfonate [27], nonionic polyoxyethylene(23) laurylether [20], Gum Arabic [22, 28], polyacrylic acid polymer [22], and cetyltrimethylammonium bromide [27], to name a few, or solvents, for instance, acetone [29]. It is worth noting that the studies on CNTs dispersion [20, 30] have shown that the most beneficial dispersion is the one with a CNT-to-surfactant ratio of 1:1–1:5.

CNTs can enhance both the compressive and flexural strength of cementitious composites up to 50 [22] and 87% [24], respectively. The addition of CNTs also improves both the fracture energy and flexural toughness [31]. Young's modulus of cement mortars containing 0.1 wt% of CNTs can be even 100% higher compared to reference samples [24]. According to SEM images, the interaction between cement hydration products and CNTs is observed [32]. CNTs increase the crack bridging capacity of cementitious composites, acting as networks between the crack and the pores [23, 31, 33]. Moreover, nanoindentation investigation indicates that CNTs contribute to a higher growth of strong C–S–H phase [30]. CNTs act as the nanofiller of voids and thus reduce the total pore volume of cement paste [21, 23, 30, 32]. Interestingly, the addition of CNTs decreases the drying shrinkage of composites. Indeed, the authors [34] attributed this behavior to the reduction of micropores. It is worth noting that the influence of CNTs on the microstructure, porosity, and thereby mechanical properties of cementitious composites is highly dependent on the quality of their dispersion within cement matrix as well as on the type of surfactant to be used. Several studies show that the addition of CNTs may also deteriorate the properties of cementitious nanocomposites [28, 29, 33].

Over the past decades, graphene—another carbon allotrope, which is a single, planar, two-dimensional carbon layer [35]—has attracted considerable attention in science and technology, while its extraordinary properties have been extensively studied by various research groups. Especially, due to its outstanding mechanical [36] and electrical properties [37], graphene has emerged as the most promising nanomaterial for smart structures. Graphene is known to exhibit the intrinsic tensile strength of 130 GPa with a corresponding strain of 0.25, while its Young's modulus may be estimated at 1 TPa [36].

Nevertheless, studies on graphene-cement composites remain, up to date, limited due to the abovementioned perplexing problem of obtaining a uniform dispersion of a nanomaterial within cement matrix. For this reason, over the past years, special attention was paid to one of graphene derivatives, that is, graphene oxide (GO). Graphene oxide is highly dispersible in water [38] and therefore, as was assumed, also in cement mix. However, several studies [39–41] show that calcium ions present in cement paste negatively affect graphene oxide dispersion due to the chemical cross-linking phenomena. To circumvent this problem, different approaches have been persuaded, including the sonication of graphene oxide with polycarboxylate superplasticizer [42, 43] or silica fume [39, 40], which provide surface modification of nanomaterial and thereby separate graphene oxide nanoplatelets from calcium ions.

However, various cementitious composites incorporating graphene oxide, with or without surface modification, have emerged as materials with improved microstructure, mechanical properties, and durability. With the dosage of 0.03–0.05 wt% of GO, the increase up to 47, 61, and 79% has been reported for compressive [44], flexural, and tensile-splitting strength [45], respectively. The strengthening mechanism of GO in cement matrix is attributed to the chemical reaction between -COOH groups attached on the GO flakes and calcium ions from calcium hydroxide present in cement; thus, a 3D network structure is formed. Moreover, graphene oxide promotes and accelerates the growth of cement hydration products due to the nucleation effect [46–48]. As a consequence of this 3D network, the microstructure of cement composites is visibly densified with a higher crystal growth and less prominent microcracks. Furthermore, also brittle crystals of ettringite are hardly observed [49]. The addition of GO remarkably refines the porosity, reducing the critical pore size and the volume of macropores [48, 50]. For the reason of reduced porosity, the incorporation of even small amount of GO into cementitious composites leads to a decreased sorptivity [50, 51]. The decrease up to 8 and 44% has been reported for initial and secondary sorptivity, respectively [50]. Therefore, cement-GO composites feature with a tremendously reduced ingress of chlorides. Even the marginal addition of graphene oxide of 0.01 wt% may effect in significant decrease of chloride penetration depth from 26 to 5 mm [51]. Interestingly, the addition of GO and its acceleration effect on cement hydration lead to a higher drying shrinkage at early stages of hydration. Nevertheless, since drying shrinkage depends on the tension of capillary pores, which are highly reduced in composites reinforced with graphene oxide, drying shrinkage after 28 days is then reduced [47].

Some attempts [19, 52] of introducing graphene nanoplatelets (GNPs) to improve the barrier properties and enhance the durability of cementitious composites have been reported. In this respect, this low-cost graphene derivative matches the performance of graphene oxide in concrete. The addition of 1.5 wt% of GNPs contributes to pore refinement, reducing the critical pore diameter and the average void size, thereby decreasing the water permeability, chloride diffusion, and chloride migration by 80, 80 and 40%, respectively [52]. It is worth noting that according to various authors, the addition of GNPs does not improve [52] or may even, to some extent, deteriorate [53] the strength of concrete.

3. Self-monitoring materials

Electrical properties of carbon-based materials in structural engineering are drawing attention of scientists for many years, giving hope for smart materials and self-monitoring structures.

One of the first attempts of using carbon-based materials in concrete was made almost three decades ago when cut carbon fibers were mixed with concrete for traffic monitoring and weighting in motion [54]. The results were promising; however, this solution had never been implemented in large scale.

The development of science and technologies during recent years has brought new nanomaterials as graphene or carbon nanotubes with even more interesting properties, also electrical. Former experiences in structural engineering materials but also in other areas of science as medicine or aviation encouraged scientists to return to the concept of self-monitoring materials for smart structures. Clearly, carbon nanotubes are the most studied carbon nanomaterial for self-monitoring applications in concrete.

Typically, various types of sensors are used to evaluate structural health, including optical fibers, strain gauges, and piezoresistive sensors. However, these sensors possess some serious limitations and disadvantages, such as high cost, poor durability, low sensitivity, and insufficient compatibility with concrete and expensive peripheral equipment [6, 55]. The new generation of nanotechnology-based microelectromechanical system (MEMS) sensors has emerged as cheaper, more compact, and easier to install sensors than traditional ones. Nanotechnology/microelectromechanical systems were used, for instance, to measure temperature and internal relative humidity of concrete [56] or to detect cracks in concrete structures [57]. Sensors for detecting the structural integrity of concrete were fabricated as wireless cement-carbon nanotube sensors embedded into concrete beams [57]. These CNTs-cement sensors have emerged as a low-cost small wireless sensor with good sensitivity, significant repeatability, and low hysteresis. Moreover, Lebental et al. [58] have developed well-aligned, ultra-thin, dense carbon nanotube membranes to be used as a vibrating membrane in a capacitive micrometric ultrasonic transducers, which could be used in the durability monitoring of porous materials. Kang et al. [59] have fabricated a long biomimetic artificial neuron sensor, with features such as low cost, simple installation, and low weight. Due to low bandwidth and appropriate strain sensitivity, it can be used for the detection of both small and large strains and cracks in concrete structures, also under dynamic loading.

Interestingly, Nanni et al. [60] have presented self-sensing nanocomposite rods to be applied as both reinforcing elements and sensors in concrete structures. The self-sensing rods are composed of an internal conductive core, that is, glass fibers embedded in epoxy resin with carbon nanoparticles (CNPs) and an external insulting GFRP skin. The nanocomposite rods have proved to be suitable for self-monitoring of concrete beams under a four-point static bending as well as for concrete cure monitoring.

The concept of weighting loads in motion came back then recently with those new materials [61]. The research team conducted tests on compressed blocks of the concrete with carbon nanotubes and registered its performance under static and dynamic loads. The authors registered changes of electrical resistance readings, proving that even micro-strains may be measured by such smart materials. This very recent work demands more calibrating studies; still, it proves high potential of nano-concrete.

Outstanding electrical properties and low cost make graphene nanoplatelets (GNPs) an attractive nanomaterial for use in smart self-sensing concrete. As demonstrated by recent studies [62], the addition of 1.6 wt% of GNPs (a surface area of 192 m^2/g, a diameter of 6.8 μm, and a thickness of 5.0 nm) decreases more than one order of magnitude the resistivity of tested composites, thus attaining the percolation point, above which GNPs form the continuous conductive network in cement matrix. Interestingly, during the piezoresistive tests under compression, it turned out that no piezoresistive reactions were detected for samples containing 1.6 wt% of GNPs, indicating that conductive network created by tunneling of GNPs is unstable under applied loading. Indeed, the addition of only 6.4 wt% of GNPs has led to a sufficient and stable response of electrical parameters under cyclic loads. Other studies by Lee et al. [63] have revealed that, for GNPs with a surface area of 352 m^2/g, a diameter of 2.6 μm, and a thickness of 2.6 nm, the percolation threshold was obtained for 3.6 wt% amount of nanomaterial. Tests on samples with different notch depths confirmed the electrically conductive characteristics of manufactured mortar.

A very interesting and novel approach for use in structural engineering is connected with the proposal of Smart Bricks for Structural Health Monitoring of existing, often historical structures endangered by hazardous loads as, for example, earthquakes [64]. Such products have the potential of creating self-sensing systems in historical structures, giving possibility for high-performance repairs and relatively cheap and invisible monitoring solution.

4. Other applications

Numerous exciting examples of antimicrobial and self-cleaning surfaces as well as energy-harvesting applications have also been reported in the last decade [6].

Recently, it has been shown [6, 65] that some nanoparticles possess tremendous antimicrobial properties and can be used to fabricate antimicrobial materials or coatings. In particular, TiO_2 nanoparticles proved to completely damage *Escherichia coli* cells after 1 week under UV irradiation of 1 mW/cm^2. Moreover, it has been reported that the addition of silver or copper may enhance the photocatalytic activity of nano-titania even under weak UV light [66]. Interestingly, Hochmannova and Vytrasova [67] have presented paints based on aqueous acrylic dispersion with the 5 vol% addition of nano-ZnO, which proved to be a better photocatalytic coatings than the one containing nano-TiO_2. The normal domestic fluorescent light was sufficient for nano-ZnO to activate the photocatalytic and microbial processes, deactivating the tremendously wide spectrum of bacteria and fungi. Furthermore, the studies on phenylpropyl type interior wall paints incorporating nano-MgO [68] have revealed that, in contrast to paints with nano-TiO_2 and nano-ZnO, nano-MgO possess a sufficient antimicrobial activity in the absence of light irradiation. In addition, the addition of silver nanoparticles to paints and coating effects in significant antimicrobial properties in case of both Gram-positive and Gram-negative bacteria [6, 69]. In case of carbon nanomaterials, SWCNTs can cause physical cell membrane damage and oxidative stress, impacting also metabolic activity and morphology of *E. coli* bacteria [70]. Grover et al. [71] have prepared laccase-based and chloroperoxidase-based paints, incorporating MWCNTs for biocatalytic coatings. These enzyme-nanotube-based paints exhibited a high bactericidal activity against different evaluated bacteria.

Apart from antibacterial surfaces, the addition of nanomaterials may also enhance the self-cleaning abilities of construction materials. Self-cleaning surfaces are mainly classified into two categories: hydrophobic and hydrophilic surfaces. As reported by previous studies [72–74], nano silica may be used to fabricate transparent superhydrophobic films and coatings on glass. The nanoporous structure made out of nano-SiO_2 also possesses antireflection properties [72, 73]. Hydrophobic surfaces were also developed with the use of carbon nanotubes (CNTs). Transparent, conductive, and superhydrophobic films incorporating CNTs were prepared on a glass substrate using, for instance, fluoropolymer-grafted MCWNTs [75] or CNTs produced by plasma-enhanced chemical vapor deposition and functionalized by a 1H,1H-2H,2H perfluorodecyl-trichlorosilane and hexane mixture [76]. Nanoparticles used typically in hydrophilic surfaces are materials with photocatalytic properties. Tan et al. [77] have revealed that transparent TiO_2 films fabricated by the growth of TiO_2 nanotube arrays on glass substrate have exhibited a higher photocatalytic activity than nanoparticulate TiO_2 thin films due to a higher surface area. Interestingly, Pan et al. [78] have presented nanofiber-based TiO_2 films with stable super-amphilicity, which possessed superhydrophilic properties even after 240 days in the absence of UV irradiation. It is worth noting that the effect of various forms of TiO_2 [79] as well as the interaction between TiO_2 and pigments has been investigated in the case of cement mortars [80]. Mortar with the addition of 3% of anatase powder and 2% of anatase suspension has emerged as a commercially attractive material with optimal photoactivity [79].

Nanomaterials as conductive materials have also the potential for energy harvesting. Tests on this issue are conducted in many research centers, not connected with structural engineering. Some of them, especially those connected with obtaining energy from mechanical actions [81] and solar [82] activity, have the potential, which could also be considered in large engineering and special structures made out of smart nanomaterials.

5. Nano-toxicity

Among all nanomaterials, the toxicity of carbon nanotubes (CNTs) draws most attention due to their fiber structure and insolubility in lungs, thus significant similarity to asbestos [83]. Evaluation of carbon nanotubes (CNTs) toxicity is an extremely challenging task, since the reactivity of CNTs is influenced by many factors, such as surface area, size and shape, structural defects, purity, chemical composition, solubilization, surface chemistry, and charge [14, 83]. CNTs may cause inflammatory, genotoxic, and fibrotic effects in the lungs, thus contributing to lung cancer [84]. In addition, exposure to CNTs may also lead to skin irritation [84]. When CNTs ingress human cells, they can accumulate in cytoplasm and contribute to cell death [14].

Graphene oxide (GO) and graphene family nanomaterials (GFNs) have a strong antibacterial and antifungal activity. However, they may also negatively affect the biological structures of cells and cause side effects. First of all, the oxidative stress is detrimental to cellular macromolecules: proteins, DNA, or lipids, just to name a few [85]. Moreover, due to sharp edges of graphene, it may damage cell membranes, thus causing the membrane destabilization [85, 86]. It is worth noting that graphene nanomaterial accumulations may be potentially toxic for certain organs, including lungs and liver [85]. Importantly, the toxicity of graphene and derivatives thereof depends strongly on the type of nanomaterial, its shape and size, purity, surface properties, synthesis method and post-producing treatment, dispersion degree, concentration, oxidative state, and functional groups [86, 87].

6. Conclusion

Nanotechnology has a high potential for applications in civil engineering. Nanomaterials such as nano-alumina, nano-titania, nano-silica, nano-magnesium oxide, nano-zinc oxide, silver nanoparticles, carbon nanotubes, or graphene derivatives may have enhanced hydration, microstructure, porosity, and thus mechanical properties and transport-related properties of cementitious composites (**Table 1**). Moreover, nanoparticles can also ensure completely new capabilities of structural composites, namely self-cleaning, self-sensing, and antimicrobial activities. Recent nanotechnological developments in civil engineering open up new avenues for the technological applications of nanomaterials in high-performance cement composites

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Nanomaterial	Effect on the properties of building materials	References
Nano-alumina	Improved mechanical properties	[8, 10, 11]
	Refined microstructure and porosity	[8, 11]
	Accelerated hydration	[8]
	Reduced water absorption	[8]
	Increased impermeability	[10]
	Improved performance at elevated temperatures	[10]
	Enhanced frost resistance	[11]
Nano-silica	Improved mechanical properties	[9, 11]
	Refined microstructure and porosity	[9, 11]
	Enhanced corrosion resistance	[9]
	Enhanced frost resistance	[11]
	Self-cleaning properties	[72–74]
Nano-titania	Improved mechanical properties	[13]
	Refined microstructure and porosity	[12, 13]
	Enhanced corrosion resistance	[12]
	Increased impermeability	[13]
	Improved performance at elevated temperatures	[13]
	Self-cleaning properties	[66, 77–80]
	Antibacterial activity	[66]
Carbon nanotubes	Improved mechanical properties	[14, 18, 20–24, 27–33]
	Refined microstructure and porosity	[14, 21, 30–32]
	Reduced shrinkage	[14]
	Self-sensing properties	[24, 25, 27, 58, 59, 61]
	Enhanced corrosion resistance	[24]
	Self-cleaning properties	[75, 76]
	Antibacterial activity	[70, 71]
Graphene nanoplatelets	Refined microstructure and porosity	[19, 52]
	Reduced water absorption	[19, 52]
	Enhanced corrosion resistance	[19, 52, 62]
	Self-sensing properties	[53, 62, 63]
Graphene oxide	Improved mechanical properties	[41–43, 45, 46, 48–50]
	Refined microstructure and porosity	[41, 42, 44–46, 48–51]
	Accelerated hydration	[44, 47, 48]
	Reduced water absorption	[50, 51]
	Enhanced corrosion resistance	[51]
Silver nanoparticles	Antibacterial activity	[69]
Nano-magnesium oxide	Antibacterial activity	[68]
Nano-zinc oxide	Antibacterial activity	[67]

Table 1. Effect of the incorporation of various nanomaterials into building materials.

as well as in structural health monitoring. However, of significant importance is to focus on new solutions, which will facilitate the use of nanotechnology in real industrial-scale applications. Moreover, a key focus for the nanotechnology of structural composites should be ensuring the comprehensive toxicological studies.

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Conflict of interest

The authors declare no conflict of interest.

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