Review Article

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Mechanical and smart properties of cement nanocomposites containing nanomaterials: A brief review

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Abstract: We report a brief review on the recent developments on smart cement nanocomposites. Cement nanocomposites containing functional nanomaterials are important class of materials for the development of sustainable civil infrastructures. Smart properties can be achieved by adding various nanomaterials, such as, titanium oxide (TiO_2), iron oxide (Fe_2O_3), graphene, graphene oxide (GO), carbon nanotubes (CNTs), carbon nanofibres (CNFs), and polymers at low weight percent (wt%) to cement. However, optimization and understanding of underlying physical and chemical mechanisms are necessary for further developments. Although, there exist huge research articles, and some reviews dealing with specific aspect over the last 10–15 years, a systematic review is necessary, encompassing both the aspects of mechanical properties as well as smart properties. In the present review, we focus on the effect of addition of functional nanomaterials to achieve smart properties maintaining basic mechanical strength at the desired level. Our review shows that addition of TiO_2, SiO_2, Fe_2O_3, CNTs, or GO in the range of <5 wt% improves mechanical strength by ~30–50% or more due to improvement in the filling of pores, bridging of gaps, and prevention of cracks. Addition of functional nanomaterials show higher photocatalytic dye degradation (~90% dye pollutant is degraded within first 1 h), higher inhibition zone of microbial growth (due to the addition of 1 wt% (or less) TiO_2, silver, copper oxide, or zinc oxide nanoparticles). Furthermore, addition of functional nanomaterials also show improvement in the impermeability, shrinkage, hydrophobicity, thermal/electrical conductivity, and piezo electricity to a significant level.

Keywords: review on smart cement nanocomposites, mechanical properties, photocatalytic, antimicrobial and hydrophobic properties, corrosion resistance and piezoelectric properties

1 Introduction

Smart cement nanocomposites are important class of materials useful for long run sustainable developments [1–6]. They display not only smart properties but retain their basic mechanical strength intact. Hence, they can simultaneously be applied for civil construction as well as for cleaner production. Various smart properties are being explored in this regard, especially, photocatalytic dye degradation, air/water pollution control, hydrophobic surface, and antimicrobial activities. Piezoelectric sensing, thermal and electrical conductivities, preventing chemical attack, or corrosion resistance have also been explored. To prepare smart cement nanocomposites, Portland cement (PC) is used as the basic ingredient. Various functional nanomaterials are being added to achieve improved mechanical properties and smart properties. A variety of PCs are existing depending upon applications, as shown in Figure 1. For example, rapid hardening cement for high strength and high shrinkage of cracks; high alumina content to withstand high temperature; slag cement for good workability and resistance against chloride ions; sulphate resistance cement; low heat PC for high strength, durability, and corrosion resistance; and pozzolanic cement for high strength, less shrinkage, and less permeation. In all the cases, various additives are responsible. Presence of nanomaterials in the cement composites not only enhance mechanical properties but also bring smart properties. They accelerate basic cement hydration and formation of calcium–silicate–hydrate (C–S–H) gel leading to improved mechanical strength. At the same time, depending upon the type of additives, specific smart property may appear. Usually, various metal oxides, metal nanoparticles, carbon nanomaterials, and polymers are added to ordinary portland cement (OPC) to modify

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Figure 1: Different types of PCs that have different application purposes.

mechanical, physical, and chemical properties. One of the key aspects of improving mechanical strength is to prevent cracks in the cement paste or concrete. Cracks may appear due to brittle nature of cement composites which may affect durability (Figure 2). Porous nature may also cause damage. Thus, maintenance is required to keep buildings, walls, bridges, *etc.*, at the safe level. Addition of functional nanomaterials may prevent the generation of microcracks, cracks propagation, and further damage. Nevertheless, due to large active surface area compared to micro and macro particles, better filling of pores is possible that may lead to stronger binding with surrounding cement constituents. Microfibres and macrofibres (large) also play a vital role, especially, in preventing microcracks and subsequent formation of macrocracks and their propagation through the bridging action (Figure 2a [7,8]). Thus, the size of cement particles and additives play crucial role for cement strengthening. Figure 2b shows a plot of surface area of various particles useful in construction industry [9]. It shows high surface area associated with nanoparticles that are useful for the preparation of high strength cement composites. Different types of additive nanomaterials are identified, such as, oxides that include titanium dioxide (TiO_2), iron oxide (Fe_2O_3), silicon dioxide (SiO_2), zirconium oxide (ZrO_2); carbon nanomaterials such as carbon nanotubes (CNTs), carbon nanofibres (CNFs), graphene, graphene oxide (GO), reduced graphene oxide (RGO); and polymers (polymethylmethacrylate; PMMA and polyvinyl alcohol; PVA) [10,11]. In the past 10–15 years, researchers across the globe have put tremendous research efforts to fabricate novel

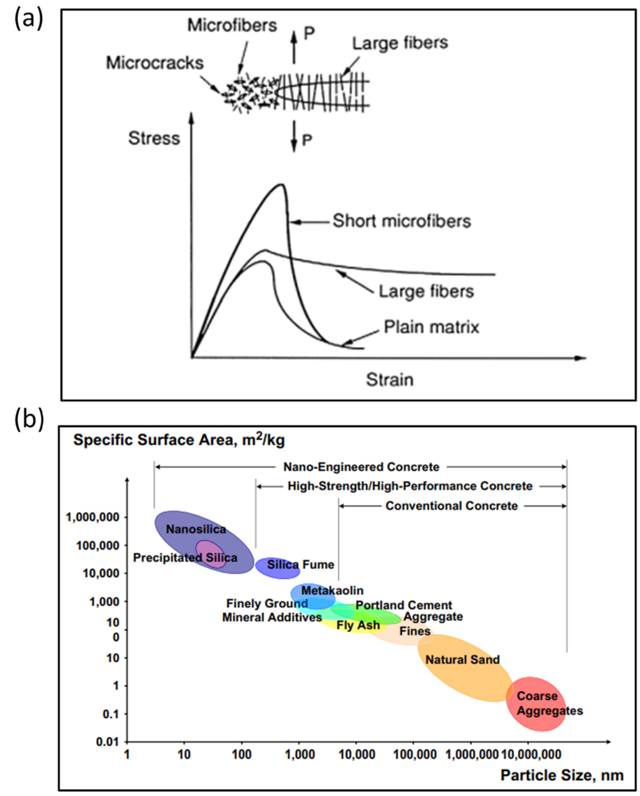

Figure 2: Relation between load and crack developed in the sample (a), and relative size of material used in construction industry (b). Figures are reproduced with permission from [7] for (a), and [9] for (b).

cement composites that contain various functional nanomaterials. Figure 3 reflects the research strength, year wise, in terms of published articles. Figure 3 is plotted using the data as obtained with the help of Google Scholar search engine. Appropriate "string" is used for literature research as

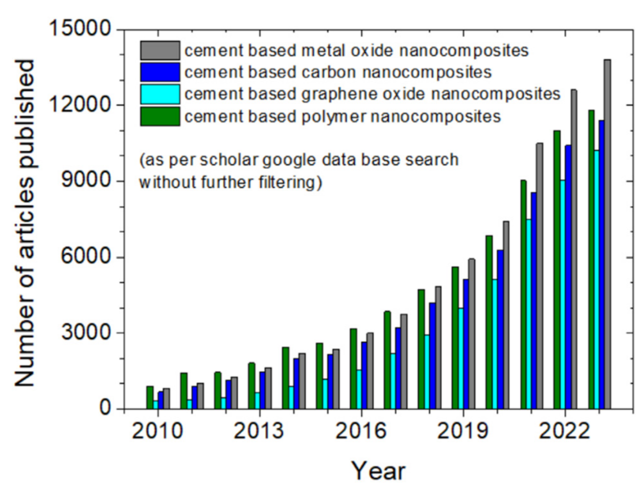

Figure 3: Year wise number of articles published on the topics as mentioned in the legend.

mentioned in the legend (with no further filtration). As evident from the figure, research interest is continuously growing over the years.

Till date, majority of the research reports focus on the simultaneous occurrence of improved mechanical properties and smart properties. To achieve smart properties, of course, basic mechanical strength must not be compromised to a large extent. It is, therefore, very important to understand the cement hydration process and improvement in mechanical strength due to the addition of functional nanomaterials. On the other hand, optimization and deeper understanding are required too to achieve specific smart property retaining basic mechanical strength intact. Hence, a systematic review dealing with both these aspects is believed to be helpful for further developments. In view of the existing reviews. which have mainly focused discussions on the specific concerns of cement nanocomposites, the present report encompasses broader aspects of cement nanocomposites containing oxides, graphene and its derivative, carbon nanomaterials, and polymers. Two main aspects are being considered: (a) basic mechanical properties (compressive and flexural strength) and (b) smart properties (especially, photocatalytic dye degradation, antimicrobial activity, hydrophobicity, and piezoelectric property). Reports available in the last 10–15 years are analysed. As in Figure 4, a methodology is followed to look at cement-based oxide nanocomposites, cement-based GO nanocomposites, cement-based carbon nanocomposites, and cement-based polymer nanocomposites. Literature reports are analysed in view of mechanical properties and smart properties. In brief, after introducing relevant cement basics in Section 2, we have introduced discussion on the mechanical properties of cement nanocomposites containing functional nanomaterials in Section 3. Effect of addition of various functional nanomaterials, such as oxides, graphene and its derivative, carbon nanomaterials, and polymers on the mechanical strength of the cement nanocomposites is discussed. In Section 4, smart properties, especially, photocatalytic dye degradation, antimicrobial activity, hydrophobicity are discussed. Smart properties, types of functional nanomaterials, dosages, and attainment level are summarized in Table 1. At the end, challenges and future scopes are outlined in Section 5.

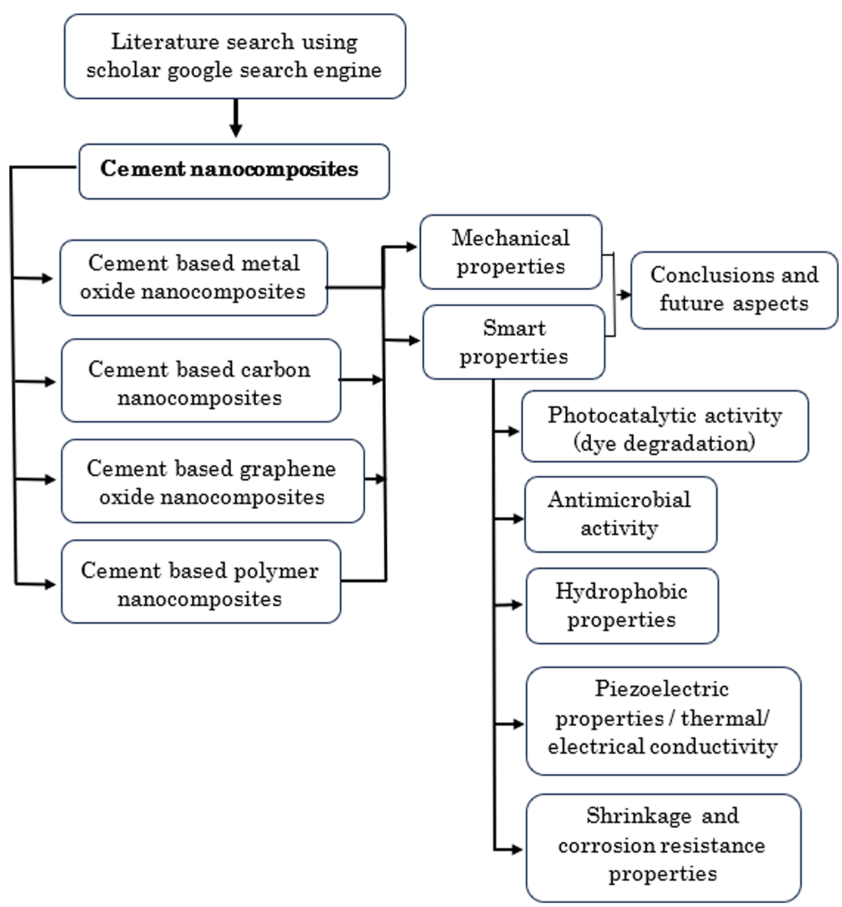

Figure 4: Flowchart of the research work conducted for the present review article.

Table 1: Cement nanocomposites, smart functionalities, additives and their dosages, and level of improvement

Cementitious composites	Specific purpose addressed	Level of improvement	Ref.
Graphene/TiO_2 nanocomposites coating on cement mortar	Photocatalytic self-cleaning and air purification abilities (RhB discoloration and NO removal under visible light) with good regeneration performance	The performance is compared among (a) pure cement mortar, (b) cement mortar coated with TiO_2, and (c) cement mortar coated with TiO_2/graphene. The 2D planar conjugated π-structure of graphene favours adsorption of target pollutants due to higher specific surface area. This results in more effectiveness of TiO_2/graphene in the composite	[80]
Nano-TiO_2 cement concrete, Nano-TiO_2 is used by internal doping method (IDM) and spraying method (SPM)	Photocatalytic degradation efficiency tested for methyl orange (MO)	Nano-TiO_2 may be used by both the methods (for better photocatalytic performance) that may depend on the type of application: IDM for pavement materials, and SPM for wall building materials	[81]
Cement composites containing Fe_2O_3, TiO_2, and copper (Cu) nanoparticles	Photocatalytic dye degradation (of Rhodamine-6G)	Enhanced dye-degradation is observed. Highest degradation rate of about 2.5 times faster (OPC containing Fe_2O_3) compared to control sample is observed	[82]
Photocatalytic additive (TiO_2) is added to mortars (aerial lime, cement, and gypsum binders)	To study degradation rate of common urban pollutant, NO_x	1% of TiO_2 addition results in reasonable degradation rate of NO_x without losing mechanical strength	[83]
Anatase-type TiO_2/cement mortar system for dye degradation	Photocatalytic activity: dye (methylene blue: MB) degradation under UV irradiation	TiO_2-mortar cementitious materials show photocatalytic activities without damaging of mechanical properties. Highest MB degradation of ~76.6% happens in 4.5 h with 1% TiO_2. Other concentration is less effective.	[84]
TiO_2-cement mortar cementitious materials	Photocatalytic activity: NO_X removal	Addition of TiO_2 shows photocatalytic activity without significant change in flexural and the compressive strength of the modified cements	[85]
Cement mortar containing Ag-TiO_2 photocatalysts	Photocatalytic dye degradation under ultra violet (UV) and visible light	Dye degradation rate: (a) For MO, it is 95.5% at 30 min under UV light (b) For MB, it is 69.8% at 40 min under visible light	[86]
Cu-TiO_2/SiO_2 photocatalyst coating on concrete-based building materials	Self-cleaning and air de-pollution performance	Addition of Cu to TiO_2 photocatalyst up to ~5% promotes photocatalytic activity Self-cleaning and air pollution reduction are tested on MB, NO, *etc.* 95% MB degradation occurs within 60 min. Photocatalytic activity decreases for Cu doping beyond 5% may be due to defect states (trap states)	[87]
CdS/TiO_2-cement-nanocomposite catalyst	Photocatalytic dye degradation	Under UV light, TiO_2–cement composites result in better dye degradation, whereas CdS–TiO_2–cement composite is more efficient under visible light	[88]
Nitrogen and carbon co-modified TiO_2 photocatalyst in cement pastes for photocatalytic activity	Self-cleaning/dye degradation upon UV-Vis light exposure	Modified TiO_2 shows better photocatalytic efficiency than unmodified TiO_2	[89]
Visible-light-driven photocatalytic cement samples containing BiOBr precursor for RhB degradation and NOx removal	Photocatalytic property on RhB degradation and NOx removal under visible light irradiation	BiOBr precursor in cement matrix shows better photocatalytic activity compared to control sample	[90]
ZnO or ZnO–SiO_2 and lignin-cement composites	Prevention or slower bacterial growth (antimicrobial study)	ZnO-enriched systems show high antimicrobial resistance, ZnO–SiO_2 shows deterioration of the antimicrobial effect, with	[91]

(*Continued*)

Table 1: *Continued*

Cementitious composites	Specific purpose addressed	Level of improvement	Ref.
		lignin showed lower growth than other systems	
Silica-titania (SiO_2/TiO_2) core-shell nanostructures-cement mortar	Self-cleaning, bactericidal, and photocatalytic properties	It acts as filler, self-cleaning and bactericidal properties under UV exposure are also observed	[92]
Antimicrobial activity of aluminium oxide (Al_2O_3), copper oxide (CuO), ferrosoferric oxide (Fe_3O_4), and zinc oxide (ZnO) nanoparticles in cement-based building materials	Antimicrobial properties	Proper mixing of metal oxide nanoparticles in cement nanocomposite is important in observing antimicrobial response. Unproper dispersion may not be effective. Furthermore, even antimicrobial response of different strains from same species may be different.	[93]
PMMA based cement composites: Addition of silver nanowires for antibacterial activity	To enhance antibacterial activity	Silver nanowires (1 wt%) will enhance antibacterial activity against aureus	[94]
Inhibition ability of growth of bacteria and fungi due to the presence of copper (II) oxide, zinc oxide, and titanium (IV) oxides in the cementitious material (cement mortars)	Inhibition ability of growth of bacteria (*E. coli* or *P. aeruginosa, etc.*) and fungi (*C. albicans*)	0.1% ZnO, 0.5% CuO, and 1% TiO_2 can be used separately for inhibition of growth of bacteria and fungi with highest inhibition with CuO. The dispersion is an important factor that may affect the workability and strength. This may even affect antimicrobial activity.	[96]
ZnO nano-needles in white cement for photocatalytic, hydrophobic, and antimicrobial property	Enhanced photocatalytic, hydrophobic, and antimicrobial property	ZnO nano-needles in white cement show significant improvement in the photocatalytic, antimicrobial activity	[97]
Cement-based composites containing PZT particles: Influence of water-to-cement ratio on piezoelectric properties	Piezoelectric properties	Piezoelectric cement (containing 30–70% PZT) with a favourable water to cement ratio (w/c: 0–20%) can improve its piezoelectric properties	[98]
Cement-based piezoelectric composites	Piezoelectric and dielectric properties	Properties depend on the interfacial microstructure between the matrix and the piezoelectric insertion	[99]
Piezoresistive properties of cement mortar doped with GNPs	Piezoresistive properties	For optimal piezoresistivity, GNP may be used in the range of 0.05–0.1%	[100]
Nanoclay and graphite in cement (0–1 wt% of cement) composite for the reduction of shrinkage	Reduction in shrinkage	Plastic shrinkage reduction by ~70% is achieved (independent of nanomaterial type)	[101]
CNTs-cement mortars	Shrinkage and bridging effects	About 0.05–0.1% of CNTs mixing reduces early stage shrinkage by ~62%. This may be due to the reduction in capillary stresses by filler and nucleation effect of smaller diameter CNTs decreasing fine pores between the hydration products	[102]
Cement mortar and concrete are prepared with distilled and electrolyzed water (30 min)	Corrosion resistance study (sodium sulphate: Na_2SO_4, sodium chloride: NaCl, and a combined mixture of Na_2SO_4 and NaCl solution)	The cement mortars and concretes prepared with electrolyzed water show less attack	[103]
Effect of nano-TiO_2 on the microstructural and corrosion resistance properties of cementitious composites	Corrosion resistance properties under different exposure of tap water, saline water, acidic solution	Corrosion inhibition efficiency is good up to 5 wt% of nano-TiO_2 for all the environments (tap water, saline water, acidic solution)	[104]
Nano titanium dioxide (nTiO_2) in EGA (expanded glass aggregates)-mortar	To enhance the mechanical properties and water resistance of cement mortar	Nano TiO_2 improves mechanical properties and water resistance ability	[105]
RGO in cement mortar	Enhancing thermal properties of cement mortar by incorporating RGO	1.2 wt% RGO doping enhances thermal conductivity and thermal diffusivity coefficient by 7.8 and 29%, respectively	[106]
RGO in cement composite	Improving electric conductivity and electric shielding property	RGO in cement composite improves electric conductivity and electric shielding property by 23 and 45%, respectively	[107]

(*Continued*)

Table 1: *Continued*

Cementitious composites	Specific purpose addressed	Level of improvement	Ref.
Waste iron oxide concentrate (IOC) is added to cement mortar	Thermal conductivity	Addition of waste IOC (30%) to cement mortar increases thermal conductivity by about 25%	[108]
Addition of nanosilica into cementitious material	Thermal stability	Considerable enhancement of thermal stability due to addition of nanosilica (5 wt%). Sample that does not contain nanosilica shows more damage at elevated temperature. Reduction in CH due to the pozzolanic activity of nanosilica seems to be the primary reason for minimum damage and higher stability.	[109]
Ionic paraffin emulsions in cement nanocomposite	To improve hydrophobicity	Addition of 4.0% non-ionic paraffin emulsion in cement mortar exhibits outstanding hydrophobicity compared to anionic and cationic paraffin emulsions	[110]
Different hydrophobic agents (stearic acid, DryCit, rapeseed oil) in cement composites (1–2 wt%)	To improve internal hydrophobicity	Water resistance in the pore protection factor test increases between 21 and 33%	[111]
Silane-based nontoxic hydrophobic agent along with waste tire rubber in integrally hydrophobic self-compacting rubberized mortar (HSCRM)	Hydrophobicity	Decrease in water absorption and increase in corrosion resistance due to better hydrophobicity	[112]
Amorphous carbon powder (ACP) in cement paste	Hydrophobicity and electrical properties	Addition of 15% ACP by weight reduces water absorption and electrical conductivity of cement paste by 23 and 65%, respectively	[113]
Tyre rubber addition to cementitious material (cement paste)	Improving hydrophobicity	Smaller grain size results in better hydrophobic characteristics	[114]
Addition of crumb rubber cement paste	Improving hydrophobicity to reduce water penetration	Rubberized cement paste shows reduced water penetration due to improved hydrophobicity of paste treated with crumb-rubber	[115]
Multifunctional cementitious composites containing GNP and silicone hydrophobic powder (SHP)	Piezoresistivity and hydrophobic behaviour	Addition of SHP (2%) shows better reduction (~15 times) of water absorption. Along with isolation effect of GNP, the SHP powder helps in improving hydrophobicity in the specimen surface and other places such as pores and cracks. This effect reduces water absorption and helps in achieving stable piezoresistivity.	[116]

2 Important basics of cement

2.1 Cement compositions

The most common type of cement in the hydraulic cement category used for construction purpose is PC which is made of various silicates and oxides. When clinker minerals and water are mixed together the hydration process results in the hardening of the mixture.

Clinker phases are:

Alite (C_3S): 3CaO SiO_2, Belite (C_2S): 2CaO SiO_2

Tri-calcium Aluminate (Celite C_3A): 3CaO Al_2O_3

Brownmillerite (Felite C_4AF): 4CaO Al_2O_3 Fe_2O_3

Limestone ($CaCO_3$) is burnt to produce CaO. This process releases CO_2 (main source of carbon dioxide emission during calcination). CaO then reacts with SiO_2, Al_2O_3 to produce 2CaO SiO_2/3CaO SiO_2 and 3CaO Al_2O_3, respectively, and with Al_2O_3 and Fe_2O_3 to form 4CaO Al_2O_3 Fe_2O_3

$CaCO_3 \rightarrow CaO + CO_2$,

$2CaO + SiO_2 \rightarrow 2CaO\ SiO_2$(or Ca_2SiO_4),

$3CaO + SiO_2 \rightarrow 3CaO\ SiO_2$(or Ca_3SiO_5),
$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow 4CaO\ Al_2O_3Fe_2O_3$.
The typical composition of PC [12] is
CaO:~65%, SiO_2 : ~20%, Al_2O_3 : ~5%, Fe_2O_3 : ~3%
along with some other compounds of minor quantity (such as MgO, SO_3, $CaSO_4$, *etc.*).

2.2 Cement dispersion

Cement dispersion plays a crucial role on initial cement hydration and microstructural properties. Water content to total available surface area of cement paste, mortar, or concrete influences heat evolution and packing [13]. Well dispersion of additives is essential to achieve better workability of cement paste, mortar or concrete, and reliable mechanical strength. Cement paste strength predominately varies depending upon w/c ratio of workable mix. It reduces as ratio increases as shown in the Figure 5 typically at 7 days of curing [14]. There are various models proposed in calculating the strength of cement mix [15–18]. Elaborate discussion is beyond the scope of present review. However, it is noteworthy that simplistic models are given earlier by Feret [15] and Abrams [16]. Subsequent improvements and/or discussions, and various other models can be found in previous studies [17,18]. Interested readers are referred to these studies.

2.3 Cement hydration and setting time

Cement hydration is exothermic chemical reaction that takes place between cement and water when mixed together. Various parameters such as water-cement ratio, casting temperature, and presence of C_3A and C_3S influence the overall hydration of cement. Furthermore, cement hydration also gets influenced by micro/nanostructures and fineness of mixed components. Reaction of C_3A, C_2S, and C_3S with water results in hydrated calcium aluminate, hydrated calcium silicate, and hydrated calcium silicate along with CH (*i.e.*, Ca $(OH)_2$), respectively. Addition of water to cement results in initiation of cement hardening. This is an important process where optimum setting time is expected, as, too slow or quick may create problem of mixing, transportation, and placing the cement mixture at the working places. Usually, 30 mins to about 10 h is considered to be ideal [14]. Setting time gets influenced by w/c ratio, admixtures, and fineness of cement. A detailed discussion on the cement hydration using predictive models based on the dissolution and water diffusion theory can be found elsewhere [19]. These models can predict accurate cement hydration and concrete's performance evolution.

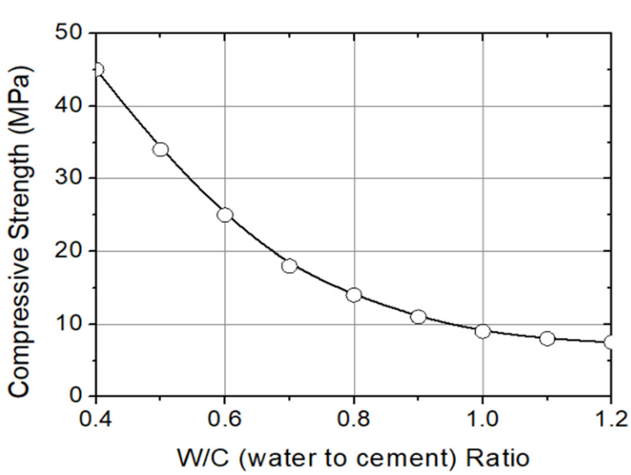

Figure 5: Influence of water to cement ratio on the compressive strength of cement mix typically at a curing of 7 days.

2.4 C–S–H gel formation in cement paste

Nanoscale building block of cement binder is C–S–H cohesive gel with no fixed composition and structure. Its formation starts when alite ((C_3S): $3CaO\ SiO_2$) or belite ((C_2S): $2CaO\ SiO_2$) reacts with water (chemical reactions are as follows: $2C_3S + 6H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + 3CH$ + heat energy (high), and $2C_2S + 4H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + CH$ + heat energy (low)) during the cement hydration process [20–23]. It is known that C_3S hydration is faster, and is responsible for early stage cement strength (within first 7 days) while C_2S reacts with water slowly, and results in latter stage (after 7–14 days) cement strength. Mechanism of C–S–H gel formation leading to cement setting is not straight forward which needs further study. Due to large surface area, cement hydration rate may get accelerated by the presence of C–S–H with increased precipitation in the capillary pores. Cement hydration and gel phase formation can be studied using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopies [24,25] to understand structural and chemical changes that occur during hydration process.

2.5 Consistency of cement paste

Cement consistency is useful to work with cement paste. It is the ability of cement paste to flow, and defined as the quantity of water required to make the cement paste of normal consistency. Vicat apparatus is used to test the cement paste consistency. Typically, 24% (wt%) water (or, if required, it may be varied from 26 to 33%) is added to 500 g of cement and mixed. Then, plunger is gently released to obtain depth of penetration within 5–7 mm from the bottom [14].

2.6 Compressive strength

Compressive strength is the signature of cement strength defined by the ratio, $f_c = F/A$, where F = maximum force applied to the specimen before break, and A = area on which the force is applied. It is the capacity of a given material to withstand loads against compression or reducing size of the specimen. Compressive strength is measured using standard sample size (for example: mould of dimension 70.6 mm × 70.6 mm × 70.6 mm can be considered for testing [14]. Test samples are cured at 3, 7, 14, 28, and 56 days. After normal drying (at ambient temperature) the sample cubes are tested for compressive strength using compressive testing machine.

2.7 Flexural strength

Ability of a material to withstand bending action due to applied load is termed as flexural strength. It is also termed as modulus of rupture. Flexural strength is a measure of tensile strength indirectly. It can be measured from a three-point loading and centre-point loading test. Flexural strength is measured using standard sample size (for example: mould of dimension 100 mm × 100 mm × 500 mm, IS 516:1959 [14]) cured for 3, 7, 14, and 28 days.

3 Cement nanocomposites containing functional nanomaterials: mechanical properties

Improvement in the mechanical strength (compressive strength and flexural strength) due to the addition of various functional nanomaterials, such as oxides, carbon nanomaterials, and polymers is a result of acceleration in cement hydration and formation of C–S–H gel, reduction in pores, and controlling in cracks and cracks propagation. While addition of TiO_2, SiO_2, and Fe_2O_3 nanoparticles (usually, at <5 wt%) shows improvement in the compressive and flexural strength due to effective pore filling and cracks reduction [26–36], the addition of GO/RGO and CNTs (<1 wt %) results in even higher compressive and flexural strength (>100%) due to accelerated cement hydration, bridging action, and controlling of cracks and cracks propagation [37–42]. On the other hand, to achieve specific properties, such as corrosion resistance and reduce permeation, polymers are added [43,44]. Mechanical properties of cement composites containing various functional nanomaterials are discussed in Sections 3.1–3.3 systematically.

3.1 Cement nanocomposites containing TiO_2, SiO_2, Fe_2O_3, and ZrO_2

Incorporation of oxide nanoparticles, especially, TiO_2, SiO_2, Fe_2O_3, and ZrO_2 into cement host improves compressive strength and flexural strength. This is due to accelerated cement hydration and subsequent C–S–H gel formation. It is usually safe to add non-toxic oxides to improve mechanical strength. For example, SiO_2 being one of the constituents of cement is added further to improve the mechanical strength of PC. Rong *et al.* [31] reported the reduction in pores and pore diameter, and showed ~50% increase in compressive strength and flexural strength by adding up to 3 wt% nano SiO_2. Liu *et al.* [32] showed ~106% increase in compressive strength and ~67% increase in flexural strength due to the addition of nano SiO_2 up to 4 wt%. The addition of nano SiO_2 results in porosity reduction and pore refinement. Recently, flexural and compressive strength enhancement was reported by Ng *et al.* [45]. They used nano-sized TiO_2, SiO_2, and Fe_2O_3 in cement mortar and showed improvement in the compressive strength in the range of 38–35%. Feng *et al.* [46] showed how nano-TiO_2 in cement reduces microcracks and surface roughness using atomic force microscopy. Acceleration in pozzolanic reactions improves microstructures of concrete. In this view, process of C–S–H gel formation plays major role in strengthening concrete [47]. Pozzolanic reaction, cement hydration, and subsequent C–S–H gel phase formation to be critically looked at for further development of smart cement composites. In the recent past, Han *et al.* [48] reported enhanced tensile and flexural strength of cement mortar, where accelerated chemical process of C–S–H formation was thought to be responsible for enhanced mechanical strength. Effect of nano-TiO_2 on hydration and shrinkage was studied by Zhang *et al.* [49]. They showed enhanced compressive strength and pore refining and shrinkage. Phase of TiO_2 may play an important role in improving the fatigue and flexural strength of cement composites [50,51]. Akono *et al.* [26] investigated the effect of nano-TiO_2 on C–S–H phase distribution within PC paste and showed increase in compressive strength by 12%. They have also shown ~30% reduction in cracks and ~22% improvement in the filling of pores and microstructure. Han *et al.* [30] studied nano silica coated TiO_2 in reactive powder concrete and showed filler action C–S–H gel formation due to pozzolanic action causing ~87% increase in flexural strength and ~12% increase in compressive strength. They also reported better inhibition of cracks.

Hematite (Fe_2O_3) nanoparticles may be considered as highly effective in improving mechanical strength due to their structural stability and possibility of physico-chemical binding and accelerating pozzolanic reaction at early stage [45,52,53]. On the surface of these nanoparticles, C–S–H gel may grow which may further act as nucleation sites for C–S–H, leading to the formation of more compact structure with reduced pores [45]. For example, Abdulabbas *et al.* [34] showed that addition of up to 5 wt% Fe_2O_3 causes improvement in the microstructures and ~75% increase in compressive strength and ~60% increase in flexural strength. Li *et al.* [52] showed experimentally that incorporating Fe_2O_3 and SiO_2 in to cement host increases compressive and flexural strength of cement mortar which could be due to the reduction in the number of pores or filling of pores by the added oxide nanoparticles. C–S–H growth is responsible for the increased compressive strength and flexural strength as reported by Kiamahalleh *et al.* [53]. It was noted that optimum wt% of nanoparticles within the cement plays decisive role in enhancing mechanical strength and microstructural properties. It was also reported that reduction in micro-cracks results in improved bonding and hence mechanical strength. Optimum dose of Fe_2O_3 was found to be ~2.5 wt% in the cement mortar, showing influential effect of preventing the formation of microcracks and their propagation [53]. Furthermore, its presence is effective too in improving water molecules accessibility to the cement C–S–H and oxygen groups of Fe_2O_3 during cement hydration [53]. Among other oxides, effect of nanosized ZrO_2 on PC was studied by Trejo-Arroyo *et al.* [54]. They reported that mortar with ZrO_2 nanoparticles showed enhanced microstructural properties with high degree of compaction and increased compressive strength by ~9%. The presence of ZrO_2 nanoparticles inhibited growth of large $Ca(OH)_2$ crystals too.

3.2 Cement nanocomposites containing GO/RGO and carbon nanomaterials

Cement nanocomposites containing graphene and GO have drawn significant research interests due to exotic properties of graphene. For example, it has excellent conductivity of heat and electricity, high Young's modulus of 1 TPa, and intrinsic strength of 130 GPa [55]. Only about 1 wt% of graphene addition to cement may be sufficient to improve mechanical strength and other smart properties. Wang *et al.* [39] incorporated about 0.05 wt% GO in cement paste and showed ~90% increase in flexural strength and ~40% increase in compressive strength. Addition of GO promotes cement hydration and decreases pore volume. Yang *et al.* [56] reported huge improvement in the compressive strength (~40%) when they added only 0.2 wt% of graphene to cement even within the aging of 3 days and 7 days. A significant improvement in the compressive strength was observed too by Cao *et al.* [57] by adding graphene nanosheets in to cement. Babak *et al.* [58] reported increase in tensile strength by the use of 0.1–2 wt% GO along with 0.5 wt% super plasticizer. The presence of GO in composite reduces the growth of crack in cement mortar [59] and influences pore structures of concrete [60]. Recently, cement composite containing functionalized GO was studied by Wang *et al.* [61]. Graphene oxide was functionalized with 3-aminopropyl triethoxysilane and amorphous SiO_2 to protect GO basal plane from alkaline environment and participate in cement hydration process. With the incorporation of 0.15 wt% functionalized GO (FGO) in the cement they saw a huge increase in flexural (~49%) strength and compressive strength (~35%). This could be due to the improvement in the bonding between the nanoparticles and cement. FGO may be considered as a future potential candidate for cement industry. There are a few recent articles that show some studies on piezoelectric properties, thermal conductivity of concrete-GO/RGO, and multi-functionalities of cement-multilayered graphene. For example, Rehman *et al.* [62] prepared graphene nanoplates (GNPs) cement composites and showed ~30% increase in load carrying capacity. At maximum compressive load, electrical resistivity drops by 42%. Recently, Zhang *et al.* [63] developed a novel self-sensing cement composite using RGO in cement. They saw improvement in the compressive strength (by ~29%), flexural strength (by ~49%), and electrical conductivity (by ~23%). A report by Sun *et al.* [64] on cement composite containing multi-layer graphene showed ~54% increase in compressive strength, 1.6 time higher shielding effectiveness, and ~7 times stronger absorption performance compared to composite without multilayer graphene.

Carbon nanomaterials such as single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) too have strong influence on the mechanical, structural, and optical properties (such as photocatalytic dye degradation) of cement composites. These are considered as next generation promising high performance materials for cement industry. Incorporation of short carbon fibres into cement reduces porosity, increases stiffness of the materials (C–S–H gel), and mechanical strength [65]. A very high increase in compressive strength of cement mortar up to 154 and 217% is reported by Yazdani and Mohanam [66] when they just incorporated only 0.1–0.2% CNTs and CNFs. In fact, carbon fibres help in arresting cracks and can show better load transfer mechanism [67]. Carbon fibres with strong interfacial formation can bridge cracks and improve surface quality by reducing pores, resulting in better bonding and C–S–H cement hydration. Addition of CNTs (0.5% CNT) along with SiO_2 (20%) increases compressive strength of cement mortar [68]. When CNT fibres and polyvinyl alcohol (PVA) are used in the composite, an increase in the flexural strength is seen, as reported by Metaxa *et al.* [69]. On the other hand, CNTs (SWCNTs and MWCNTs) in cement mortar also show considerable improvement in the compressive and flexural strength [70–74]. When MWCNTs and CNFs are added together to cement mortars, a significant enhancement in the flexural strength (~106%) is seen, as reported by Gdoutos *et al.* [70]. Uniform dispersion of carbon nanomaterials is necessary for improving mechanical strength. Effective dispersion can be made by functionalizing carbon nanomaterials with hydrophilic functional group such as COOH. Cement mortars containing COOH functionalized MWCNTs are studied by Sarvandani *et al.* [71]. Various amounts of MWCNTs (0.05–0.4% by weight) are added to cement mortars, and compressive and flexural strengths are studied at different environmental conditions. They have seen an increase in flexural strength which is a result of better bridging action. Furthermore, it is noteworthy that filler action may refine pores, improve mechanical and microstructure properties, and inhibit cracks by better bridging actions with accelerated cement hydration and formation of C–S–H [72,74].

3.3 Cement nanocomposites containing polymers

To protect infrastructures from chemical attack or environmental damage, cement composites containing polymer/epoxy may suitably be applied [75–79]. However, it needs to be ensured that polymer containing cement composites maintain required level of mechanical strength (optimum dosage of polymer is crucial for enhancement). A study by Imtiaz *et al.* [75] has shown that flexural strength of polymer impregnated concrete (PIC) is higher than OPC. Another report by Eskander *et al.* [77] has shown how cement-polymer composite (recycled polystyrene foam waste in cement) may be considered as effective for corrosion resistance. Corrosion resistive polymer (fibre-reinforced polymer sheets) modified concrete is reported recently by Tu *et al.* [78] showing significant improvement in the resistance to chloride ion attack. Rustum and Eweed [79] have studied cement mortar containing 1–9 wt% of PMMA. They have found enhanced flexural and compressive strength with best enhancement at ~5 wt% of PMMA. The enhancement is attributed to the possible coordinate bonds between C=O groups of PMMA and cement ions. Chen *et al.* [76] have shown better controlling of pores due to polymer loading. Polymer–cement nanocomposite may provide better strength and durability due to improved pore structure. Liu *et al.* [43] have studied the polymer-modified concrete (polymer modifier: styrene-butadiene rubber latex, polyacrylic ester emulsion, and organic silicon waterproof agent) and have shown improvement in pore structure and compactness. They have also shown improvement in the resistance to chloride ion penetration.

4 Smart properties of cement nanocomposites

Cement nanocomposites with smart properties are of recent interests due to the potential applications in self-cleaning and photocatalytic activities [80–90], antimicrobial activities [91–97], piezoelectric (lead zirconate titanate: PZT) smart properties [98–100], corrosion and shrinkage [101–104], mechanical, thermal, and electrical properties [105–109], and hydrophobic coatings [110–116]. This smart sensing has now been possible due to technological developments and discovery of novel functional nanomaterials. Smart materials show unique signature property in response to the external excitations. Primarily, the addition of nanosized materials to OPC would not only improve the basic mechanical strength of the cementitious materials but also exhibit certain smart properties. In the present review, photocatalytic activity and dye degradation, self-cleaning, and antimicrobial properties are specifically discussed for composites containing oxide materials such as TiO_2, Fe_2O_3, SiO_2, CuO, ZnO, Al_2O_3, and CdS as main additives (they are potential photocatalysts and antimicrobial agents). For example, Chen *et al.* [117], in a recent review, presented details of photocatalytic aspects of cement-based materials. Photocatalytic activity of cement-based materials containing high band gap oxides may be enhanced by co-addition of two different nanomaterials. High band gap materials are less effective for visible light absorption. Hence, for visible light driven (SUN as natural source) photocatalysis, lower band gap materials may be suitable. However, one needs to look at the aspects of electron-hole recombination (less recombination is preferred) too. Therefore, proper selection is necessary during the preparation of cement nanocomposites. For example, hybrid copper dozed zinc oxide (Cu-ZnO) is added in cement mortar along with graphitic carbon nitride (g-C_3N_4) by Liu *et al.* [118] to show higher efficiency and stability of photocatalytic activity. The composite is effective for visible light. Combination of GO and TiO_2 in cement composites shows highly enhanced photocatalytic dye degradation (94%) compared to composite containing TiO_2 only [119]. Furthermore, they are highly effective for inhibiting microbial growth. GO is reported to be effective for antimicrobial activity [120]. Therefore, cement composite containing GO may be considered as potential candidate for photocatalytic activity (due to higher absorbance of light) as well as antimicrobial activity (effective oxidation of biomolecules) [121]. Due to the presence of oxygen containing groups (carboxylic acid (–COOH), hydroxyl (–OH), and epoxy (–COC–)) uniform dispersion is possible that may result in higher mechanical strength at the same time. Other carbon nanomaterials, cement composites containing carbon nanomaterials, such as, CNTs (especially functionalized CNTs) show smart properties (thermal and electrical conductivities) as well as higher mechanical strength due to bridging effect [122,123]. Uniform dispersion of carbon nanomaterials (graphene, GO, CNFs, and CNTs) in cement composites is challenging which must be looked at seriously [124]. On the other hand, smart properties, such as, hydrophobicity, impermeability, corrosion resistance (chemical attack), and piezoelectricity are important too that need further attention. For example, for realization of cleaner surface, hydrophobic property must be studied in depth. Various hydrophobic materials, such as, tyre-rubber, crumb-rubber, amorphous carbon powder, ionic paraffin emulsions, rapeseed oil, and stearic acid may be added. Similarly, for enhancing piezoelectric response, one can add PZT [98]. Thus, for enhancing various smart properties, one needs to add various functional nanomaterials. However, optimization (optimum content) is required to achieve such properties without affecting mechanical strength significantly. In Table 1, we have summarized some cement nanocomposites, their smart properties, dosages of additives, and level of achievements.

5 Conclusion, challenges, and future aspects

In the present review, we have discussed recent developments of cement nanocomposites containing oxides (nano TiO_2, Fe_2O_3, SiO_2, and ZrO_2), carbon nanomaterials (CNTs, SWCNTs, and MWCNTs), graphene and its derivatives (GO, RGO, and GNP), and polymers (PMMA, PVA, and crumb rubber). Addition of these nanomaterials usually in the range of 1–5 wt% or less shows considerable improvement in the compressive strength and flexural strength. Higher dose of additives may lead to the reduction in mechanical strength (higher dosage may lose effectiveness due to phase separation). Increase in cement strength is caused by the acceleration in cement hydration and formation of C–S–H gel. Nanoparticles may act as additional nucleation site for C–S–H gel to form leading to more compact microstructures. Nanoparticles can fill pores, bridge gaps, prevent microcracks generation, and cracks propagation. This can improve overall cement binding and hence mechanical strength. Various smart properties, especially, photocatalytic dye degradation, self-cleaning/air pollution control, antimicrobial activities, hydrophobicity, piezoelectricity, and corrosion resistance are discussed in detail. Interestingly, these cement nanocomposites show smart properties keeping their mechanical strength at desired level.

To realize smart cement nanocomposites, one needs to add various oxide nanomaterials, carbon nanomaterials, and polymers. Every functional nanomaterial has a specific purpose for being added to OPC. While metal oxides may play important role in filling of pores and strengthening binding, functional carbon nanomaterials, especially, carbon fibres, CNTs may actively participate in bridging the gap and preventing crack developments. However, mechanisms of improvement are poorly understood. Focused research is necessary to unveil the underlying mechanism. Even the basic understanding of C–S–H gel formation, chemical kinetics and structural phases are not very clear till date. Challenges lie in developing cementitious materials with smart properties and optimization to retain basic mechanical strength intact. Uniform dispersion of nanomaterials in cement composites is needed, therefore, it must be looked at critically. Production of nanomaterials, their functionalization, cost effectiveness, and toxicity (safe level of exposure) have been other set points that need attention.

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