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ENHANCING CONCRETE PROPERTIES USING NANO MATERIALS

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Abstract: As most sciences, material science was obviously affected by Nanotechnology and its promising applications. Many researchers had investigated the improvement in concrete mechanical and durability properties induced by incorporation of nano-materials. This paper reviews the effect of various nano-materials on mechanical, durability and microstructure characteristics of concrete. It highlights the current and potential applications of nano-materials in concrete. This will contribute to existed knowledge about nano-modified concrete and pave the way for wider acceptance and implementation in public infrastructures.

1 INTRODUCTION

Concrete is one of the most consumed bulk material by mankind. Its remarkable features such as ingredients availability, mold-ability and high strength with low cost make it the first choice for various construction applications. Traditional concrete grading (ranges from 25 to 45 MPa) [1] were popular as it was providing adequate strength for normal types of structures. Starting from 1960 newly types of structures had special requirements concerning strength, which consequently required a new types of concrete with high performance concrete to meet the new design requirements [1].

As most kinds of sciences' and research fields, material field has been hit by new kinds of technology. Nano technology is an example which enabled scientists to study and control matters at nano scale. This provides promising opportunities to effectuate many achievements at many fields through imaging, measuring and manipulation. Dimensions are considered to be at nano scale when it's ranging approximately between 1 and 100 nm. It's unimaginable to feel how small that is while a human hair is approximately 100,000 nm wide.

Nano technology showed a great potential through utilizing nanoparticles to improve materials' characteristics and consequently materials' abilities and behaviours. Construction materials were greatly impacted by nano technology applications. Concrete had a great fortune of studies to develop a non-traditional generation of cementitious composites. Several studies on implementation of nanoparticles in cementitious composites have found promising improvement in mechanical properties and durability.

In this paper, various nanoparticles and/or nanotubes that are being used in concrete will be reviewed. In addition, a brief discussion for their potential in improving concrete mechanical properties, durability and micro structure characteristics will be conducted. This would pave the way for more future work targeting enhancement of concrete properties using nano materials.

2 BETTER UNDERSTANDING OF CEMENTITIOUS COMPOSITES USING NANO TECHNOLOGY

As for any technology or application, it's a must first to study and understand well all characteristics of the media of implementation. Hence, the best way to utilize such this technology is explored. Moreover, understanding the structure at nano-level assists in identifying the important processes related to production and use of construction materials [2].

Advances in instrumentation industry had provided scientists and engineers with the needed tools to study or control matters at nano scale. Electronic microscopy as an example allowed engineers to image the morphology of cementitious composites' ingredients **Fig. (1)**, as well as the formation of hydration products. This allows knowing kinds of defects that should be controlled, or kind of improvement that should be processed to enhance performance.

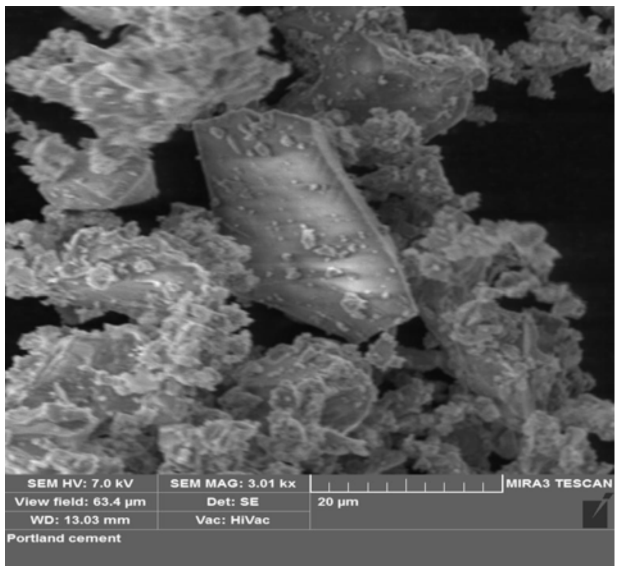

Figure 1: SEM image to show the cement particles amorphous natures

3 MICRO STRUCTURE OF CEMENTITIOUS COMPOSITES

The performance of cementitious composites was found to be influenced by nano voids between cement as a binder and aggregate particles. Also, the formation of nano size calcium silicate hydrate particles has a significant effect. Controlling these features through adding nano particles, a dense micro structure might be obtained while well dispersion of nanoparticles is insured.

Singh et al. (2012) stated that adding 5% of nano silica to cement paste increased the compressive strength with about 64% and 35% than that of mixtures without nano materials at ages of 1 day and 28 days respectively [3]. Also, dense and more compact microstructure as well as less (Ca OH) crystals was reported [4,5].

Li et al. (2017) investigated the microstructure of cement mortar with nano silica (NS) and nano Fe2O3 (NF). Specimens were prepared using 3, 5 and 10% of nanoparticles replacement by weight of cement with w/c ratio of 0.5. The average particle size of NS and NF was 15 and 30 nm, respectively. Crushed specimens after compression test were examined by SEM. It was clear that nanoparticles performed as a filler material for nano voids. Also, NS incorporation had contributed to hydration process producing more C-S-H gel, which resulted in enhanced microstructure [6]

4 NANO MATERIAL PRODUCTION APPROACHES IN NANO TECHNOLOGY

Guterrez reported that all materials can be transformed into nano size [7]. Whatever the production approach used, it's important to insure that the chemical composition will remain the same as the original material. Two approaches for nanoparticles production were developed.

4.1 Top to down approach

In this approach, milling is the main technique used to produce nanoparticles through resizing. The pioneer of this technique was John Benjamin when he produced oxide particles in nickel super alloys [8]. This process is performed using high energy balls milling machine. However, the uniformity and quality of nanoparticles produced are inconsistent, while many factors are influencing the production process such as types of balls, number of balls and speed of milling [9,10,11]. Milling may also be used for blending more than one kind of particles adopting them in a new composition.

4.2 Bottom to up approach

It's known as molecular nano technology or molecular manufacturing process, which involves more indirect applications such as synthesis or chemical formulation [12]. It is like an assembly process while materials are engineered from atoms or molecular components. Bottom to up approach gives more uniform nanoparticles where atoms are always supposed to be in good order. However, this approach is better than top to down approach. But it is still having expensive operational cost and it requires chemical application expertise [7,13,14].

5 APPLICATION OF NANOPARTICLES IN CEMENTITIOUS COMPOSITES

5.1 Nano Silica

Beside its pore filling effect obtained because of small size (4-400 nm diameter), nano silica ($nSiO_2$) is supposed to have high pozzolanic reactivity because of its significant high surface area. Which make it one of the most widely used materials with cementitious composites to improve its performance.

5.1.1 Performance

Additional calcium-silicate-hydrate (C-H-S) particles are formed when nano silica is added to concrete. These particles are working through spreading between cement grains to form denser C-H-S phase. This process is not limited on grain surface only, but also in the pore space resulting in acceleration of early cement hydration [15]. Nano silica particles also contribute to improve workability of fresh concrete through its round shape while using minimum dosage of superplasticizers [16].

Most of researches agreed that addition of nano silica greatly increase water demand, which is an ascribed to the significant high surface area [17]. Filling effect of nanoparticles in general can explain this as a result of packing of particles, decreasing the spaces in between, and consequently decreasing the free water, which is a reason for higher internal friction between solid particles [18].

5.1.2 Fresh Properties

Senff et al. (2009) incorporated 9 nm silica particles with ratios up to 2.5% by cement weight in cement paste. They reported a reduction in the initial and final sitting time. This phenomenon can be probably associated with the high pozzolanic reactivity of nano silica [17]. Concrete samples were studied by various researchers, the same phenomena of sitting time reduction was observed for tested samples incorporated by various quantities of nano [19].

Pawel Sikora et al. (2015) used nano silica particles with different sizes (100 and 250 nm). Cement mortar samples were prepared containing (1, 3, and 5%) by cement weight for each size, and they reported that the higher ratio of nano silica used the less consistency of fresh mortars obtained, especially for bigger size [20].

5.1.3 Mechanical properties

As age, water content and other factors, concrete ingredients influence concrete strength as well. Concrete with nano silica was reported to achieve better mechanical properties than that of normal concrete

Ye Qing (2007) studied the influence of nano silica addition on properties of hardened cement paste as compared with silica fume. The same ratios up to 5% replacement of cementitious materials were used for both samples, cement paste with nano silica had showed higher compressive strength [21]. Concrete with nano silica was also reported to achieve higher compressive strength, bending strength and abrasion resistance than normal concrete. Gengying Li (2004) studied the effect of nano silica addition to pozzolanic concrete. Behaviour of high volume fly ash concrete with nano silica was observed up to 720 day. It was reported that nano silica incorporation (4% by weight of cementitious materials) increased the compressive strength at the early age as well as the later age [22]. Naji Givi, A. N. et al. (2010) studied the effects of different sizes of nano silica (15 and 80 nm) with different ratios up to 2% and constant water/binder ratio of 40%. The findings indicated that 15 nm is optimum size to use with concrete, higher compressive strength up to 24% was obtained, split tensile strength was improved by 100% and flexural strength was improved by 55% [23]

5.1.4 Durability

Calcium hydroxide, aluminates and un-hydrated cement, all these composites are resulting in a porous cement paste matrix, usually through being embedded into the hydration product (C-S-H) gel [24]. This gel is formed mainly of silicate chain with varying lengths held together by layers of calcium [25,26]. Although this gel with its exceptionally good mechanical properties and which usually representing (50-70% by volume) [27], it still a heterogeneous structure when we are talking about the whole cement paste, this heterogeneity gives the cement paste its porous nature. Gaitro, J. J. et al. (2008) studied the effect of nano silica addition on the reduction of calcium leaching, they found that addition of nano silica has a great potential in porosity reduction measured in term of pore volume [28].

5.2 Nano ZrO_2

Zirconium dioxide (ZrO_2) nanoparticles have been rarely investigated. Several works are needed to introduce this new material as partial cement replacement [29], and to cover the lake of knowledge about the benefits that might be achieved through its implantation in cementitious composites.

5.2.1 Pore structure

When nano ZrO_2 particles are uniformly dispersed in concrete with the convenient amount, it’s supposed that the distances between them are small enough to restrict the formation of $Ca(OH)_2$ which consequently will result in a decrease of shrinkage and creep of cement matrix [29]. Also due to their high activity, nano ZrO_2 particles can contribute to improving cement hydration. Then it can be stated that nano ZrO_2 particles can contribute to improve pore structure of cementitious composites through playing the filler part, accelerate and improve cement hydration because of its high activity and control the size of formed $Ca(OH)_2$ to be smaller. Mohamed Hossein et al. (2011) studied the effect of nano ZrO_2 addition with average particle size of 15 nm, concrete samples were prepared with incorporation of nano ZrO_2 with ratios of (0.5, 1, 1.5 and 2 % by wt.) as a replacement of cement, reduction in total specific pore volume specially for harmful pores and multi harm pores with sizes (50-200 nm) and (> 200 nm) respectively [30] was obtained. And it was reported through results obtained that 0.5% replacement is the optimum for porosity reduction and average pore diameter as well [29].

5.2.2 Fresh properties

Ali Nazari et al. (2010) investigated concrete incorporated by nano ZrO_2 particles of average size of 15 nm, 0.5, 1, 1.5 and 2 % were used as replacement ratios by weight of nanoparticles to study its effect on fresh concrete properties, water to binder ratio of 0.4 was used for all mixtures, It was observed that initial and final sitting times were reduced [31], which is a proof of high reactivity of nano ZrO_2 particles giving it good potential as an addition to enhance concrete properties.

5.2.3 Mechanical properties

Benefits of nano ZrO_2 particles incorporation were investigated with different types of concrete. Ali Nazari and Shadi Riahi (2010) investigated the effect of nano ZrO_2 particles addition on mechanical properties of high strength self-compacting concrete, ratios up to 5% replacement by weight of cementitious materials were used. They reported about 50% increase in compressive strength, 75% increase in split tensile strength and 57% increase in flexural using 4% replacement [32].

Mohamed Hossein et al. (2010) studied the incorporation of nano ZrO_2 particles in concrete. An increase up to 12.5% of 28 day compressive strength was reported with addition of 1% of nano ZrO_2 particles replacement by cement weight. Higher ratios were found to reduce the compressive strength. However, flexural strength has recorded about 32% increase for the same age [29].

5.3 Nano TiO_2

Due to low cost, safety and chemical stability [33], Titanium dioxide (TiO_2) (also known as titania) became a widely used material in many fields. Recently, many investigations were made to study the benefits of using titania with cement based materials from different points of view. Zhang et al. (2010) investigated concrete samples incorporated by nano TiO_2 Up to 5% replacement of cement weight, the author concluded that 1% replacement is optimum as it showed 18 and 10% enhancement in compressive strength and flexural strength, respectively [34].

Baoguo Ma et al. (2015) studied the effect nano TiO_2 on toughness and durability of cementitious materials, mortar specimens were prepared using 1, 2, 3, 4 and 5% of nano TiO_2 as cement replacement ratios, water to cement ratio was fixed at 0.58. At 28 day, 3% replacement had shown 68% increase in tensile strength and 62% increase in flexural strength [35].

Another significant enhancement that nano TiO_2 particles can give to concrete is coming through its potocatalytic capacity [16].

5.3.1 Self-cleaning

Dives in Misericordia" in Rome designed by Richard Meyer was the first clear example of a building using nanotechnology for self-cleaning application. Its concrete elements were made of white cement with nano TiO_2. Visual monitoring was recorded for six years after construction, trivial changes in the white color of the outside surface were recorded [36], which is an indication of the developed self-cleaning feature. Mortars containing TiO_2 were studied by Diamanti et al. [37] and he concluded that contact angle between water and solid surfaces containing TiO_2 nanoparticles was reduced by almost 80%.

5.3.2 Air pollution reduction

Nanoparticles incorporation showed great contribution in air pollution reduction. For example, for indoor air, Majer et al. [38] had measured the reduction in air pollution for indoor air using gypsum plastering containing 10% TiO2. PICADA project [39] tested air pollution on a macro-scale model for a sealed car park of area (322 m2) and the ceiling was painted with TiO_2 based painting, a pollution of a single car was then applied. Results showed that TiO_2 based paint had an effective photocatalytic capacity in pollution reduction.

5.3.3 Bacterial capacity

As an application of using nano TiO_2 particles, they are studied from the bactericidal capacity point of view and great results were found. Since fungi are responsible for mycotoxins growth [40], Saito et al. studied the addition of TiO_2 with an average size of 21 nm finding that 120 minutes were sufficient to kill all the bacteria [41].

5.4 Nano **Alumina**

Nano aluminum oxide (Al_2O_3) also known as nano alumina has many significant good properties such as hardness, which make it a clear choice for researchers to study its effects on cement based materials. It can be produced by both approaches of nano materials production.

Ali Nazari et al. (2010) examined concrete samples containing 0.5, 1, 1.5 and 2% by weight of cement, water to cement ratio of 0.4 was fixed for all mixtures, workability was recorded to be dramatically reduced by increasing alumina content. The author recommended 1% replacement as optimal level achieving 15% increase in compressive strength with respect to control sample [42].

Another study by Hase et al. (2015) was investigating the effect of colloidal nano alumina to show its benefits as a filler material, 1, 2, 3 and 4% cement replacement ratios were used with fixed water to cement ratio of 26%. 3% level was found to be optimum while 20.7% increase in compressive strength, 32.25% increase in split tensile strength and 37.3% increase in flexural strength were recorded [43].

5.5 Carbon nanotubes (CNT)

Carbon nanotubes are considered to be a modified form of graphite where carbon atoms are bonding together in hexagonal pattern to form sheet [44], this sheet then is rolled up to be a single-walled carbon nanotube (SWNT) with diameter (0.4-10 nm), or multi sheets (10-100) are rolled up together to be multi-walled carbon nanotube (MWNT) with diameter (4-100 nm) [45,46].

5.5.1 Synthesize of carbon nanotubes

There are three known methods to synthesise carbon nanotubes, Laser ablation, electric arc discharge or chemical vapour deposition (CVD), which is classified as a preferable method. That came through its less cost, higher purity and ability to control diameter, length and alignment. [47,48,49].

5.5.2 Fabrication of CNT-cementitious composites

Due to its extraordinary properties like aspect ratio (100-250000) [50], tensile strength (11-63 GPa) [51], carbon nanotubes have been studied by scientists to show the significance added to concrete mechanical properties through using carbon nanotubes. Great advantages might be obtained from smaller diameter and aspect ratio of CNT which helps to achieve crack bridging through wide distribution in the matrix with reduced spacing, also different behaviour in bonding mechanism is expected while the diameter is close to thicknesses of (C-H-S) layers of hydrated cement [44].

A key parameter that should be taken into consideration while using carbon nanotubes is good dispersion. Due to its small diameters and extremely high aspect ratio, carbon nanotubes tends to agglomerate while dispersing, then good dispersion should be achieved through sonication to deliver acoustic energy through a liquid.

Also, chemical treatment (functionalizing) as a successful technique may be utilized through using agents (typically strong acids) to form functional groups on CNTs surface, creating kind of covalent interfacial bonding with cement products [50]

5.5.3 Mechanical properties and porosity

Li et al. (2005) tested mortar samples incorporated by 0.5 % by cement weight of CNT, chemical treatment was through using sulphuric (H_2SO_4) acid and nitric acid (HNO_3) under 3 hours sonication, 19% increase in compressive strength was recorded, 25 % increase in flexural and 64 % reduction in porosity was obtained as well [52].

Rashid et al. (2012) studied two types of carbon nanotubes, short (1.5 μm) and long (10-30 μm), ratios of 0.04, 0.1 and 0.2 % by cement weight were used for short CNT while only two ratios up to 0.1% was applied for long CNT, that's b cause of high tendency of long tubes to agglomerate resulting in difficult dispersion. It was concluded that 0.2 % of short CNT was optimal as it showed 15% increase in modulus of elasticity, 45% increase in ultimate strain and greatly significant increase for flexural strength at 28 days.

6 CONCLUSION

- Nano technology showed a great potential for utilization of nanoparticles to improve materials characteristics.
- Advances in instrumentation industry had gifted scientists with the needed tools to control matters at the nano level.
- Besides being reactive with hydration products, nanoparticles also play the filler part to produce denser composites.
- Bottom to up approach still better than top to down although the latest is cheaper.
- Nanoparticles can significantly contribute to enhancement of concrete properties through its unique small size and reactivity.

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