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Nano-modification in digital manufacturing of cementitious composites

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7.1 Introduction

As new construction technologies emerge, their development requires nonconventional approaches, which include using innovative functional components. The history of concrete technology has seen several significant leaps forward by adopting this strategy. A well-known example is the development and introduction of superplasticizers in the 1970s which opened the doors for high-performance concrete (Mehta & Aietcin, 1990). Later, during the 1990s and 2000s, mineral additions and supplementary cementitious materials became increasingly essential for the development of ultra-high performance concrete (Acker & Ulm, 2013). However, in recent years it has become clear that the highest demand for innovation in concrete is not in its mechanical properties, but in its digital manufacturing (Attaran, 2017). This new approach is quickly becoming a strong candidate for future construction technologies, and even for extra-terrestrial endeavors (Matsumoto et al., 1992; Reches, 2019).

However, conventional materials appear to have limited resources to offer for further enhancing the digital manufacturing capabilities. Therefore there is a dire need for adopting nonconventional material-based solutions, for which nanomaterials stand out for the development of this additive manufacturing technology (Khan et al., 2020).

As defined by ASTM (ASTM & F2792–10, 2010), additive manufacturing is “a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies.” Until now, main techniques in the context of digital concrete manufacturing include layer extrusion (contour crafting, 3D concrete printing), particle bed printing (D-shape, binder jetting, or sand jetting), formwork printing (mesh mold), and temporary supports (flexible formwork, knitted textiles) (Wangler et al., 2019), as shown in Fig. 7.1. Detailed classifications of digital fabrication with concrete and descriptions of each specific technique are given in (Buswell et al., 2020; Reiter et al., 2020; Wangler et al., 2019). Extrusion-based method is the most popular and investigated 3D printing technology with concrete so far (Buswell et al., 2018; Marchon et al., 2018;



ETHZ – Mesh mold: method for producing the mould for creating wall structures in-situ (construction). The technology is defined by an automated assembly process using welding of discrete bar lengths.



LU – double-curved panels: method for producing panel structures as discrete parts (manufacturing). The technology is defined by the contiguous operation of layer-wise additive manufacture by material extrusion of a build and a temporary support material.



TU/e – bridge parts: method for producing parts from composite material (manufacturing). The technology is defined by the continuous operation of layer-wise additive manufacture by material extrusion, with the simultaneous entrapment of a steel wire within the extrusion.



HuaShang Tengda - wall: method for producing reinforced wall structures in-situ from composite material (construction). The technology uses two contiguous processes: placement of discrete reinforcement and continuous operation of layer-wise additive manufacture by material extrusion.



ETHZ - SDC: method for producing column structures as parts from composite material (manufacturing). The technology is defined by the continuous operation of material extrusion, with an option to simultaneously modify the extrusion cross-section.



d-Shape – 3D forms: method for producing freeform parts (manufacturing). The technology is an additive manufacturing process based on binder jetting (commonly referred to as 'particle-bed') in the field.



ApisCor – formwork: method for producing permanent formwork for casting wall elements in-situ (construction). The technology deploys additive manufacturing using material extrusion to create a formwork. Reinforcement is conventionally placed and casting completes the element.



TU Delft – Flexible mold: method for producing panel structures as discrete (manufacturing). The technology is defined by three processes in series: mould creation, casting a flat panel and then deformation during curing using a CNC pinbed.

Figure 7.1 Main techniques for digital fabrication with concrete.

Source: Adapted from Buswell, R. A., da Silva, W. R. L., Bos, F. P., Schipper, H. R., Lowke, D., Hack, N., Kloft, H., Mechtcherine, V., Wangler, T., & Roussel, N. (2020). A process classification framework for defining and describing Digital Fabrication with Concrete. *Cement and Concrete Research*, 134. <https://doi.org/10.1016/j.cemconres.2020.106068>.

Wangler et al., 2016). Remarkable attention from both academia and industry has been given to extrusion-based 3D concrete printing (3DCP) during the last decade. Many companies in the Netherlands, for example, Royal BAM Group, CyBe, Twente Additive Manufacturing, and Bruil, are attempting to implement this technology in practice.

3DCP is the digital concrete manufacturing technique under focus in this study. The development of printable cementitious composites is possibly the most critical aspect in 3DCP. Compared to mold-cast concrete process, several essential material parameters need to be controlled in 3DCP process, that is, pumpability, extrudability, buildability, and others (Le et al., 2012; Lim et al., 2012). Conventional material-based technology appears to have limited resources to offer for further enhancing the capabilities of 3D printing. Therefore there is a dire need for adopting nonconventional material-based solutions for which nanomaterials can play a vital role.

Controlling the rheology is the key to successful 3DCP, as achieving dimensional stability and the minimum required mechanical properties in green state are the main challenges. Furthermore, achieving the required strength development rate and enabling smart monitoring of the 3DCP are the other goals that are desired in designing such materials. Recent research shows that successful modification of cementitious materials can be achieved by incorporating nanomaterials in the material design for the enhanced fresh and hardened state properties. In this chapter, a summary of these developments is compiled in the light of potential applications, safety issues, and technological challenges.

7.2 Implementation of nanomaterials in extrusion-based 3D concrete printing

7.2.1 Printing processes and required material behaviors

A typical 3DCP setup, which consists of three primary components, namely, a deposition setup (three-/four-axis gantry-based, or six-axis robotic system), a control unit, and a material extrusion system (ram extrusion-based or rotor and stator-based printing setup and printhead), is illustrated in Fig. 7.2. The working mechanism of 3DCP is explained as a layer-wise construction process without a formwork (Lim et al., 2012; Wolfs et al., 2019). Because of the absence of formwork, the cementitious materials for 3DCP are expected to show a unique material behavior compared to the conventional mold-cast concrete. Specifically, the fresh cementitious materials should meet contradicting rheological requirements, that is, sufficiently flowable (low initial yield stress) under the shear during pumping and extrusion, and high shape retention and structuration rate at rest after deposition to build the layered structure (Chen et al., 2020; Marchon et al., 2018).

To date, two main printing strategies have been employed by most of the studies in the context of 3DCP. The first one is defined as the extrusion of highly stiff or sufficiently stiff material without using additional energy or adding reactive agent in the printhead (Mechtcherine et al., 2020), which is the most common printing

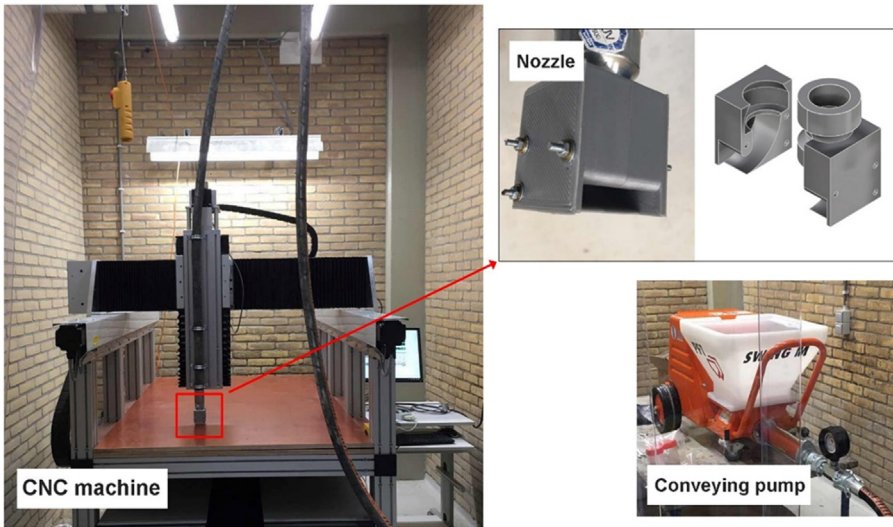


Figure 7.2 Extrusion-based 3D concrete printing setup at TU Eindhoven.

Source: Adapted from Chen, Y., Chaves Figueiredo, S., Li, Z., Chang, Z., Jansen, K., Çopuroğlu, O., & Schlangen, E. (2020). Improving printability of limestone-calcined clay-based cementitious materials by using viscosity-modifying admixture. *Cement and Concrete Research*, 132, 106040. Available from <https://doi.org/10.1016/j.cemconres.2020.106040>.

approach (see Kazemian et al., 2017; Le et al., 2012; Nerella et al., 2019; Panda, Lim, et al., 2019; Rahul et al., 2019). In this case, the printability of fresh mixture is dominated by its thixotropy. For a fresh cementitious material, the yield stress is not the same at dynamic (flow under shearing) and static (after deposition) states. The dynamic and static yield stresses are defined as the minimum stress to stop flow under shear and the stress necessary to initiate flow from rest, respectively (Marchon et al., 2018). The magnitude of the difference between dynamic and static yield stresses is regarded as thixotropy (Marchon et al., 2018; Perrot et al., 2016). A low dynamic yield stress is required to guarantee the ease of pumping and extrusion, whereas a high static yield stress is essential for constructing a layered structure. From the microstructure perspective, the static yield stress development of fresh cementitious materials is dominated by the flocculation of particles and ongoing hydration. During the pumping and extrusion processes, the links between particles are broken under constant shearing, which reduces colloidal suspension viscosity. After deposition, the viscosity of material at rest is recovered since the interparticle links are rebuilt (Panda, Ruan, et al., 2019; Roussel, 2018; Roussel et al., 2012). The addition of nanomaterials in printable mixtures (nano-clay and nano-silica) can promote this re-flocculation process (see Fig. 7.3), which has been reported by a few recent studies (Kruger et al., 2019; Panda, Ruan, et al., 2019).

In contrast, the second printing strategy is known as set-on-demand printing, which was proposed and developed by (Gosselin et al., 2016; Marchon et al., 2018; Reiter et al., 2018, 2020). The flowable mixture with a low initial yield stress close

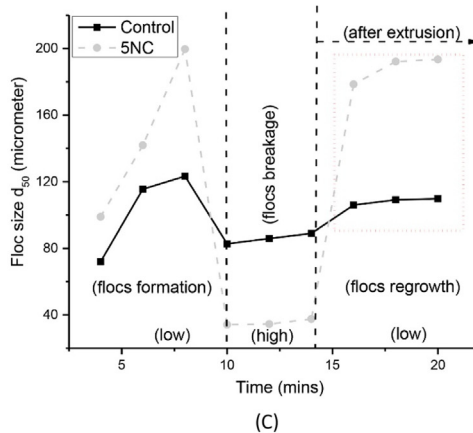
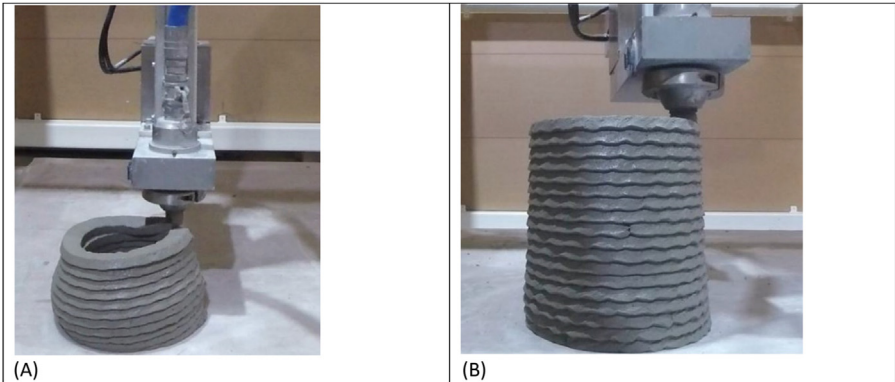


Figure 7.3 Buildability assessment of (A) Control mixture (without nano-clay) and (B) 5NC mixture (containing 0.5 wt.% (of binder) nano-clay). (C) Flocculation characterization—floc size under low and high shear rates.

Source: Adapted from Panda, B., Ruan, S., Unluer, C., & Tan, M. J. (2019). Improving the 3D printability of high volume fly ash mixtures via the use of nano attapulgite clay.

Composites Part B: Engineering, 165, 75–83. <https://doi.org/10.1016/j.compositesb.2018.11.109>.

to that of the self-compacting concrete can be easily transported through the hose to the nozzle. The reactive agent, that is, accelerator, or other fast-setting slurries, is injected and mixed with the fresh cementitious materials in the printhead (Mechtcherine et al., 2020). Consequently, the deposited fresh mixture can reach a very high stiffness because of the addition of reactive agents. Unlike the first printing strategy, the change of yield stress does not rely on the material thixotropy. Nanomaterial is not the key ingredient in this process; therefore this strategy is not discussed further.

7.2.2 Nanomaterials as thixotropic agents

Nanoparticles, typically with a particle size smaller than 100 nm, exhibit significant influences on the rheology of concrete, for example, increasing the stiffness and viscosity of fresh concrete even at a low dosage (Kruger et al., 2019; Senff et al., 2009). In recent years, it has been found that nanoparticles can be employed as thixotropic/thickening agents for 3D-printable cementitious materials (Kruger et al., 2019; Panda, Ruan, et al., 2019; Panda, Mohamed, et al., 2019). Until now, nanomaterials such as nano-clay, nano-silica, and nanocalcium carbonate have been attempted to be used in 3DCP. A summary of using these nanomaterials as thixotropic agents in 3D printable cementitious materials is shown in Table 7.1. As shown

Table 7.1 A summary of using nanomaterials as thixotropic agents in 3D printed cementitious materials.

	Nano-clay (highly purified attapulgite clay)	Nano-silica	Nanocalcium carbonate
Chemistry (phase compositions)	Si–(Mg, Al)–O	Si–O	CaCO ₃
Particle size	30 nm diameter, 1.5–2 μm length	15–20 nm	~ 150 nm
Morphology	Rod-like/fibrous shape	Spherical and porous particles	Granular shape
Effect on 3D printing	(1) Increase yield stress and plastic viscosity. (2) Enhance shape stability and buildability. (3) Improve thixotropy (accelerating green strength development without compromising flowability).	(1) Thickening effect. (2) Increase yield stress, particle (re-) flocculation rate, and structuration rate (structural build-up). (3) Enhance shape stability and buildability.	Enhance shape stability, buildability, and structural build-up.
References	Kazemian et al. (2017), Marchon et al. (2018), Moeini et al. (2020), Panda, Lim et al. (2019), Panda, Ruan et al. (2019), Panda et al. (2020), Rahul et al. (2019), Yuan et al. (2018), Zhang et al. (2018)	Kruger et al. (2019), Mendoza Reales et al. (2019), Yuan et al. (2018)	Chu et al. (2021), Yuan et al. (2018)

in Fig. 7.3, the addition of such nanomaterials could primarily improve shape stability, buildability, thixotropy, and structural buildup of fresh cementitious materials (Mendoza Reales et al., 2019; Zhang et al., 2018), which may be attributed to the agglomeration and high water absorption of nanoparticles (Khayat et al., 2019; Nazar et al., 2020). On the other hand, nanoparticles could fill the gap between cementitious particles, increasing the packing density, which consequently reduces the dynamic yield stress and plastic viscosity of fresh cementitious materials (Khayat et al., 2019). However, nanomaterials generally display a very high specific surface area (SSA)-to-volume ratio, which significantly decreases the free water content, adversely affecting the fluidity of fresh mixtures (Nazar et al., 2020). Thus it is difficult to predict the influence of nanomaterials on flowability, which may be varied using different dosages or types of nanomaterials.

Among the nanomaterials listed in Table 7.1, nano-clays appear to be the most generic ones employed to improve the 3D printability of fresh cementitious materials. Generally, nano-clay is a common class name, which can be further specified as attapulgite, bentonite (montmorillonite-based), kaolinite, halloysite, sepiolite, and contaminated clays depending on their chemical composition and particle morphology (Marchon et al., 2018; Nazar et al., 2020). The initial attempt (Kazemian et al., 2017) of using nano-clay (highly purified attapulgite clay) in printable concrete was made by researchers from Contour Crafting group at the University of Southern California. Recent studies on employing attapulgite nano-clay as the thixotropic agent in 3D-printable cementitious materials are given by (Panda, Lim, et al., 2019; Panda, Ruan, et al., 2019). Unlike the nano-silica or calcium carbonate with a round/granular particle shape, attapulgite nano-clay exhibits rod-like particle morphology.

7.2.3 Comparison between polymeric viscosity modifying admixtures and nanomaterials

In 3DCP, polymeric viscosity modifying admixtures (VMAs), including cellulose-ether derivatives and anionic polyacrylamides (Marchon et al., 2018), can be used as thixotropic agents, which exhibit the high capacity to catch water molecules and increase the dynamic viscosity of the cement paste (Palacios & Flatt, 2016). In many available 3DCP recipes (see Chaves Figueiredo et al., 2019; Chen et al., 2018; Rahul et al., 2019), both superplasticizers (mainly polycarboxylate ether superplasticizers) and cellulose-ether-derived VMAs (such as hydroxypropyl methylcellulose) were utilized for adjusting the rheology and 3D printability of fresh mixtures. The issues of incompatibility between two polymers must be highlighted. The addition of cellulose-ether-derived VMAs could compete with superplasticizers to adsorb onto the surface of particles, which affects the dispersion of superplasticizers (Khayat & Mikanovic, 2011; Palacios & Flatt, 2016). Besides, the nonadsorbed polymers could increase the viscosity of the pore solution, resulting in depletion flocculation. The competitive effects between superplasticizer and VMA may increase yield stress and plastic viscosity (Palacios & Flatt, 2016), which can significantly affect pumpability and extrudability. Using nanomaterials (nano-silica) as

thixotropic agents may also affect the compatibility between the cement and superplasticizers. The yield stress of fresh cementitious materials and the demand for superplasticizers are significantly increased by increasing the dose of nanomaterials (Sonebi et al., 2015). However, the presence of superplasticizers could contribute to the uniform distribution of nanoparticles, which was discussed in Section 7.4.1.

Furthermore, the addition of polymeric VMAs may perturb the hydration of cement, for example, prolonging the induction period, reducing the reaction rate in the acceleration period, and decreasing the maximum heat release. The negative effect of cellulose-ether-derived VMAs on cement hydration has been reported by many previous studies (Chen et al., 2020; Palacios & Flatt, 2016; Pourchez et al., 2006, 2010). As explained by Pourchez et al. (2010), cellulose-ether-derived VMAs could strongly be adsorbed on hydrated phases, that is, C–S–H and portlandite, which inhibits the growth of these hydrates. However, using nanomaterials may not adversely affect cement hydration. The presence of nanomaterials could introduce an additional amount of nucleation and/or hydrate growth surface for consuming the ions from dissolved anhydrites, which can accelerate the structural buildup and hydration (Palacios & Flatt, 2016; Roussel et al., 2019; Sanchez & Sobolev, 2010). Therefore in comparison with polymeric VMAs (especially cellulose-ether-derived VMAs), nanomaterials may be a better thixotropic agent for developing 3D-printable cementitious materials when retardation is an issue.

7.3 Effects of nano-additions on fresh and hardened state of concrete

The addition of nanoscale materials to concrete can be broadly divided into two categories, carbon-based and noncarbon-based. As cement relies on the reaction and hydration of Ca–Si–Al systems, it is natural that many efforts focus on the addition of nano-sized oxides based on calcium, silicon, or aluminum (and the combinations thereof). On the other hand, novel materials such as carbon nano-tubes (CNTs), graphene oxide (GO), and carbon nano-fibers (CNF) display advanced mechanical and electrical properties, which are sought after additions to concrete. As carbon-based additives have much higher aspect ratios, these are usually added in much smaller quantities, for example, 0.1% of binder mass, while noncarbon-based additions are typically added in values of 1%–5% of binder mass.

7.3.1 Nano-silica

Nano-silica is the cheapest and the most consumed nano-addition by the construction industry (Chithra et al., 2016). It can be found as a powder or as a suspension. The average particle size varies between 8.5 and 15 nm (Pavan Kumar et al., 2021), its chemical composition is SiO₂

However, any nanoparticle presents a much higher SSA than the other components of concrete, as stated in the previous section. Thus workability of the mix is

considerably affected. Furthermore, the properties of the material can only be tailored if uniform dispersion is achieved (Li et al., 2004). Although nano-silica is considered a zero-dimensional addition, it also suffers from this disadvantage because the grains tend to flocculate. As with other additions, researchers have successfully used superplasticizers (Senff et al., 2012), ultrasonication (Wang et al., 2015), superabsorbent polymers (Pourjavadi et al., 2012), and the application of the addition in suspension (Safi et al., 2018) as means to mitigate the effects on workability. Additionally, the high SSA improves reactivity, which has the adverse effect of reducing the setting time of the mix (Abhilash et al., 2021).

The improvement in compression strength of concrete boosted by nano-silica is because of two reasons: the pozzolanic reaction of the material, which takes place in the same manner than silica fume; and the filler effect, which aids the diminishment of voids (Abhilash et al., 2021). Research has also shown that flexural strength (Zhang et al., 2016), permeability (Pavan Kumar et al., 2021), freeze-and-thaw resistance (Gonzalez et al., 2016), and steel–matrix bond (Ismael et al., 2016) are improved by the addition of nano-silica.

7.3.2 Nano-titania

Nano-titania is the second most common nanoparticle additive for concrete (Mendes et al., 2015). These are relatively easy to obtain and are available in varying sizes, with average particle diameter ranging from 25 to 600 nm. Its typical chemical composition is TiO_2 .

The effects in the fresh state of concrete are similar to nano-silica, with the additional effect that nano-titania was found to increase the heat of hydration considerably (Nazar et al., 2020).

Although this addition also provides the standard improvement of mechanical properties, its main application is the development of “self-cleaning” concrete. Chen and Poon (2009) described in details the photocatalytic effect in such concretes, which can convert organic pollutants and oxides (such as NO, NO_2 , and SO_2) into harmless components using only UV radiation from daylight. This, however, should not be taken as literally self-cleaning, as the material still requires common cleaning, just less frequently. As the main advantage is only present on the surface, there are also commercial coatings available for concrete.

7.3.3 Nano-clay

Nano-clay is a white powder with dimensions depending on the parent mineral silicate. Many studies focus on nano-montmorillonite because of its different structure. In fact, this is a 2D addition with platelet shape, about 1 nm thickness and 70–150 nm width (Norhasri et al., 2017).

In the fresh state, this addition also increases viscosity and flocculation. However, the increase in shape stability of the fresh mix combined with the overall improvement in buildability makes this a very promising material for 3D printing of concrete (Nazar et al., 2020; Panda, Ruan, et al., 2019).

Nano-clay has certain pozzolanicity and acts well as filler, but it was shown to work better in combination with other additions. Al-Rifaie and Ahmed demonstrated that the combination of nano-silica and nano-clay is far more effective on the improvement of mechanical properties, having doubled the compression strength and quadrupled the tensile strength with respect to reference mortar samples (Al-Rifaie & Ahmed, 2016).

7.3.4 Nano-alumina

Nano-alumina is another white powder material, with a chemical composition of Al_2O_3 .

Its influence on the fresh state of concrete is similar to all other nano-additions given its particularly high SSA. One notable exception is that it can be used as a hydration retarder (Bastos et al., 2016), as alumina has preferential reaction during the very early ages (Krishnaveni & Senthil Selvan, 2021).

Besides the improvement in compressive and flexural strength, it strengthens the bond between concrete and steel reinforcement by 25% (Ismael et al., 2016). In addition, it was found that at a 3% dosage, it can be used as replacement to binder, still improving the overall mechanical behavior and durability properties (Nazari & Riahi, 2011).

7.3.5 Other mineral additions

Many other nanomaterials have been added to concrete in order to change its properties. However, most research focuses on the four nanomaterials mentioned earlier, because of their availability and cost. Yet, some new additions are worth mentioning because of their unique properties.

Nanocalcium carbonate has been found to combine a number of advantages of other additions. It provides a much more consistent control of concrete flowability to be used in digital manufacturing (Chu et al., 2021). It also provides enhanced strength, while reducing shrinkage during hydration (Cai et al., 2016). Finally, it drastically reduces the loss of water at temperatures as high as 800°C (Salih et al., 2020). It is expected that more research will be devoted to this material once its manufacturing and distribution becomes more widespread.

In a similar manner that the use of silica fume grew interest in nano-silica for the construction industry, the use of metakaolin generated interest in nano-metakaolin. This has, nonetheless, been studied at a much slower pace because of the low availability of kaolin in certain countries (Norhasri et al., 2017). Similar to nano-clay, this material is composed of amorphous alumina and silica; however, its structure comprises long-order hexagonal layers (Zhang et al., 2010). This addition increases the compressive and flexural strength of concrete considerably and has an optimal dosage ranging from 4% to 12% (Abdel Gawwad et al., 2017; Nitish et al., 2020). However, further research must be conducted for acquiring insights into the exact reaction mechanism and its effects on shrinkage before this material is popularized in construction (Zhan et al., 2020).

Nanomagnesia or nano-MgO is another relatively new additive for concrete. This has been used as a shrinkage reducer, decreasing as much as 80% in a dosage of 7.5% of cement mass (Polat et al., 2017). This is particularly useful in mass concrete, as this is an expansion agent that requires less water than usual alternatives (Shah et al., 2015). Still, the contributions to mechanical properties are not well understood as some researchers have found contributions to compressive strength as low as 1%–8% (Polat et al., 2017), while other researchers claim an increase of 80% in strength with only 1% addition of the material (Moradpour et al., 2013).

Another new addition gaining popularity is nano-zinc oxide. This addition has a distinct capacity of inhibiting the hydration of C_3S and C_2S , thus considerably increasing the induction period previous to initial setting of the cement. Liu et al. (2019) reported quantities as low as 0.2% in mass replacement of cement quadrupling the period before setting. As these particles do not react with cement or increase reactivity, the gains in compression and tensile strength are small, only caused by the void filling effect (Garg & Garg, 2021). However, concretes with ZnO addition have also been reported to gain photocatalytic properties. While TiO_2 is more efficient at degrading NO_x components, ZnO shows a much better performance against bacterial activity, even at night when no UV source is available (Kumar et al., 2021). As biodeterioration of constructions remains an open problem, it is expected this addition to find niche applications in the coming years.

7.3.6 Carbon nano-tubes

CNTs can be single- (diameter = 1–3 nm) or multiple-walled (diameter = 10–40 nm), both with a typical length of 1 μm . The elastic modulus of this material is close to 1 TPa, while the tensile strength varies between 11 and 63 GPa and the elongation at break is about 12% (Yu et al., 2000).

However, the bond of CNTs with cement products was found to be very weak, which hinders the reinforcement capacity of the addition (Fattah et al., 2015). Furthermore, acquisition remains costly, and dispersion requires special surfactants or sonication (Nazar et al., 2020).

Therefore optimal dosage varies between 0.1% and 0.2%, which leads to a modest improvement of mechanical properties. Similarly, researchers also found modest improvement in residual mechanical properties after high-temperature exposure and overall higher maximum temperature before failure (Afzal & Khushnood, 2021). For the improvement of bond with reinforcement, CNTs are found to be more effective than nano-silica, with an increase up to 50% (Song et al., 2020).

Nonetheless, the main application for CNTs in concrete is not on the enhancement of mechanical properties but on previously neglected properties. Additions as low as 0.05 wt.% in binder can drastically increase the capacity of self-sensing (Suchorzewski et al., 2020) and thermal sensing (Zuo et al., 2021), which can further be used for damage monitoring. In addition, this material also allows for electrical heating in concrete, which can be used to protect pavements from freeze-thaw damage (Choi, 2021). Finally, a much higher dosage (1%–3%) can create a

material with good service life under extreme polarization, which would be immune to chloride attack (Qiao et al., 2015).

As research progresses, it is expected that the use of CNTs in concrete will increase proportionally to the decrease in production cost or with the advent of better dispersion methods.

7.3.7 Carbon nano-fibers, graphene oxide, and carbon black

While CNTs' production price does not decrease, a few alternative solutions arise as additives for cementitious materials. CNFs are cylindrical graphene structures with a diameter of 70–200 nm and a length of 50–200 nm (Yazdani & Mohanam, 2014), displaying a far smaller aspect ratio than CNTs. This material is much weaker than CNTs ($\sigma_t \cong 8\text{GPa}$) and much easier to disperse.

At the same addition level with CNTs, it shows superior improvements in compressive and flexural strength (Danoglidis et al., 2016; Yazdani & Mohanam, 2014) and improves electrical and thermal properties at the same rate (Gomis et al., 2015). The main drive for the research and use of this material is the production cost, which is 50 times cheaper than for CNTs (Yazdani & Brown, 2016). As such, this is growing as a more viable alternative for addition.

GO is competitive with CNTs because of its cheaper production cost and higher dispersibility in water (Bastos et al., 2016). The former a 2D surface, which works as a nucleation site for C–S–H, improving the overall mix reactivity (Babak et al., 2014). An addition as low as 0.05% can increase the compressive strength by 30% and flexural strength by 60%, while also producing a ductile material (Pan et al., 2013). Furthermore, at higher quantities (0.1%), it has been shown that GO makes possible the design and use of 100% recycled aggregates concrete (Devi & Khan, 2020). It is also possible to design GOs with hydrophobic properties, then it is applied as a coating material, decreasing water absorption, capillary absorption and chloride ingress considerably (Habibnejad Korayem et al., 2020). However, some researchers (Dalal & Dalal, 2021) have reported problems with excessive shrinkage, which requires further study.

Finally, carbon black (CB) is formed from the incomplete combustion of carbonaceous materials, creating amorphous carbon molecules with open carbon bonds (Bastos et al., 2016). Because of this method of production, this material is much cheaper than the other options cited in this section. While CB does not improve the mechanical properties of concrete considerably, it can improve the electrical, thermal and self-sensing properties (Masadeh, 2015). As such, researchers (Wen & Chung, 2007) looked into replacing 50% of carbon fibers by CB and found that the conductivity could be maintained at the same level while the material price was lowered. In a similar fashion, it can also be used for electrical heating of concrete in cold climates, which allows for casting in negative temperatures (Çınar et al., 2020).

Fig. 7.4 is presented as a short summary of the main nano-additions and their contribution to the hardened state properties of concrete.

Nanomaterial	Nanoparticles									Carbon based			
	Nano-SiO ₂	Nano-Al ₂ O ₃	Nano-Fe ₂ O ₃	Nano-CaCO ₃	Nano-metakaolin	Nano-clay	Nano-MgO	Nano-TiO ₂	Nano-ZnO	Carbon nano tubes	Graphene oxide	Carbon nano fibres	Carbon black
Compressive strength and pore-filling	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Flexural strength	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Freeze and thaw resistance	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
Steel-matrix bond	Green	Green	Red	Red	Red	Red	Red	Red	Red	Green	Red	Red	Red
Hydration accelerator	Green	Red	Red	Green	Red	Red	Red	Green	Red	Red	Red	Red	Red
Hydration retarder	Red	Green	Red	Red	Red	Red	Red	Green	Red	Red	Red	Red	Red
Shrinkage reducer	Red	Red	Red	Green	Red	Red	Green	Red	Red	Red	Red	Red	Red
Photocatalytic	Red	Red	Red	Red	Red	Red	Red	Green	Green	Red	Red	Red	Red
Hydrophilic coatings	Red	Red	Red	Red	Red	Red	Red	Green	Red	Red	Red	Red	Red
Hydrophobic coatings	Green	Red	Red	Red	Red	Red	Red	Red	Red	Red	Green	Red	Red
Strain-sensing	Red	Red	Red	Red	Red	Red	Red	Red	Red	Green	Red	Green	Green
Thermal sensing	Red	Red	Red	Red	Red	Red	Red	Red	Red	Green	Red	Red	Red
Electrical heating	Red	Red	Red	Red	Red	Red	Red	Red	Red	Green	Red	Green	Green
Cathodic protection enhancer	Red	Red	Red	Red	Red	Red	Red	Red	Red	Green	Red	Red	Green

Figure 7.4 Main contributions for concrete by nano-additions.

Source: Adapted from Bastos, G., Patiño-Barbeito, F., Patiño-Cambeiro, F., & Armesto, J. (2016). Nano-inclusions applied in cement-matrix composites: A review. *Materials*, 9(12). <https://doi.org/10.3390/ma9121015>.

7.4 Challenges with using nanomaterials as additives

7.4.1 Dispersion of nanomaterials

Uniform dispersion is the main challenge when using nanomaterials in cementitious materials for 3DCP. The rheology of fresh cementitious material can be strongly influenced by the dispersion of nanomaterials. Insufficient dispersion can lead to a severe reduction in workability and weak flow consistency of fresh mixtures, which essentially limits their application (Nazar et al., 2020). Different nanomaterials show various particle morphologies, categorized as zero-, one-, and two-dimensional (0D, 1D, and 2D) nanoparticles. The dispersion of different nanomaterials with different geometries is dissimilar. As Habibnejad Korayem et al. (2020) reported, because of the lower complexity of particle geometry, 0D nanoparticles (e.g., nano-CaCO₃, TiO₂, ZnO, and SiO₂) are much easier to be dispersed than 1D and 2D nanoparticles. It is quite complex to properly disperse 1D nanoparticles (e.g., highly purified attapulgite clay and nano-CNTs) because of their bundling and entanglement. In contrast, uniform dispersion of 2D nano-sheets (e.g., nano-graphene) is extremely difficult due to their high surface energy.

For improving the dispersion of nanomaterials, sufficient energy is required to break down agglomerated particles initially. After that, the particles need to be stabilized via chemical modifications, for example, steric and electrostatic repulsion, to avoid their re-agglomeration (Korayem et al., 2017). The methods applied to enhance the dispersion of nanoparticles are discussed by (Korayem et al., 2017; Parveen et al., 2013). Both mechanical and chemical approaches can be employed. In many cases, the combination of two approaches was conducted. As summarized by Korayem et al. (2017), high-shear mixing, mechanical stirring, ultrasonication, and ball milling are the common mechanical approaches to disperse nanoparticles in aqueous solutions and cement composites. Among them, the ultrasonication method appears very frequently in literature. Applying a proper ultrasonication energy can effectively reduce the agglomeration of nanoparticles. This method is already employed to disperse CNTs (Nochaiya & Chaipanich, 2011; Zou et al., 2015), nano-CaCO₃ (Kawashima et al., 2014), nano-titania (Yousefi et al., 2013), and nano-silica (Sobolev et al., 2009) for use in cementitious pastes.

The chemical approach focused on the physical and chemical surface modifications of nanoparticles, which is generally performed after breaking down agglomerates via mechanical methods. Surface active agents, also known as surfactants, are usually employed in the physical surface modification of nanomaterials (Korayem et al., 2017). Surfactants used for physical surface treatment of nanoparticles can benefit solution stabilization through the mechanism of electrostatic repulsion and/or steric hindrance for reducing attractive Van der Waals forces between particles (Korayem et al., 2017; Lewis, 2000). As the most common surfactant in the industry, superplasticizer is used for this purpose (see Fakhim et al., 2015; Sobolev et al., 2009). However, it is worth noting that the addition of some surfactants may adversely affect cement hydration (Marchon et al., 2016). Besides, chemical surface modification is also utilized to disperse nanoparticles. As the most typical chemical treatment, functionalization is executed for attaching functional groups to the surface of hydrophobic nanoparticles to improve their hydrophilic properties (Korayem et al., 2017). This method is occupied for the dispersion of CNTs (Li et al., 2005, 2007; Zhu et al., 2003) and graphene/GO (Singh et al., 2011; Zhao et al., 2014).

7.4.2 Safety issues

Except for the high cost and uncertainties in long-term material performance, a critical concern impeding the use of nanomaterials in construction industry is their adverse biological and toxicological effects (Van Broekhuizen et al., 2011). According to earlier works (Buzea et al., 2007; Karlsson et al., 2008; Lam et al., 2006; Spitzmiller et al., 2013; Xia et al., 2009), most of engineered (carbon-based, metal-containing, and nonmetallic) nanomaterials are confirmed to have toxic effects. Spitzmiller et al. (2013) pointed out that it is quite challenging to prevent the release of nanomaterials into the environment, which may be from the structure construction, throughout the use of structure, to the end of its service life (deconstruction and disposal). Thus, the consideration and approaches are essential to

respond to the effect of nanomaterials on the health of construction workers and users, and the environment at all stages of the life cycle (Lee et al., 2010). For developing and using nanomaterials in a green and less toxic way, Spitzmiller et al. (2013) proposed a number of suggestions. First, tuning down the toxicity of nanomaterials during the manufacturing process. For example, blending 1%–10% of iron doping in nano-ZnO can reduce its toxicity. Similar approaches are expected for other nanomaterials. Second, yielding the universal design rules for green nanomaterials. Third, employing high throughput screening to test various nanomaterials in different doses, time points, and assay systems. Fourth, the research regarding the fewer environmental and health impacts should be prioritized. It suggests the tight cooperation between all related researchers at the beginning of new nanomaterials development and application.

7.5 Conclusions and future prospects

In extrusion-based 3DCP, nanomaterials are employed as thixotropic agents to rapidly increase viscosity of fresh mixture at rest (after deposition). Nano-clay (highly purified attapulgite clay) is the most frequently reported nanomaterial for improving the 3D printability of fresh cementitious materials. Compared to polymeric VMAs, nanomaterials can accelerate the structural buildup and hydration of cementitious materials.

While nano-clay improves printability, a number of other nano-additions have been successfully incorporated in concrete mixes to vastly enhance its hardened properties. Most materials have the common effect of increasing compressive and tensile strength. However, specific additions contribute to novel applications such as hydrophobic coatings, photocatalytic effect, electrical-heating, cathodic protection enhancement, which presents great prospects for more durable concrete.

The main challenge with using nanomaterials in 3D printable cementitious materials is the uniform dispersion of nanoparticles. Mechanical, chemical, or combined dispersion approaches can be applied to nanoparticles with different geometries (0D, 1D, or 2D). For 0D nanoparticles, mechanical methods, including high-shear mixing, stirring, ultrasonication, and ball milling, are commonly used. For 1D and 2D nanoparticles with high-complexity particle geometries, it seems that chemical approaches, that is, physical and chemical surface treatments, are required after the particle agglomeration is broken down by mechanical methods.

The three main obstacles for the implementation nano-modification in the digital manufacturing of a cement composites remains the price, availability, and ease of use. The price is usually controlled by the production processes. As mentioned in Section 7.3, several advances in the generation of nanoparticles have been reported recently (Bastos et al., 2016; Chithra et al., 2016; Nazar et al., 2020; Yazdani & Brown, 2016), which contributes for cheaper materials. Availability is often changed by market demand, which means that ease of use is key for the adoption of this technology, which was discussed in Section 7.4.1.

Nevertheless, the incentive to use nanomaterials in concrete is considerably strong. Governments and companies are pushing for better, more durable and more sustainable constructions (Lélé, 1991; Palacios-Munoz et al., 2019), which require concrete with enhanced properties and diminished cement consumption (Peris Mora, 2007). To achieve this, mix optimization and the replacement of normal supplementary cementitious materials by nanomaterials is seen as the most successful strategy (Ghafari et al., 2015). Thus it is likely that research and applications for nano-additions, especially in digital manufacturing, will keep expanding until natural adoption by the construction market.

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