JOURNAL OF MATERIALS & CONSTRUCTION

Journal of Materials and Construction
ISSN 2734-9438
Website: www. jomc.vn

Chemical admixtures used in 3D printing of building materials

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KEYWORDS

Chemical admixture
Digital manufacturing
Extrusion printing
Structuration
Thixotropy
Early strength
Shrinkage

ABSTRACT

Chemical admixtures present the key to successful 3D printing technologies. Moreover, many similarities between admixtures for dry-mix mortar and 3D printed mortar exist. This paper highlights current technologies and provides an outlook into which technologies might be required in the future. Generally, the kind of admixtures differ, depending on the type of 3D printing applied: extrusion, shot-crete or printing in particle bed. As of today, about 90 % of actual work uses extrusion printing. In extrusion, immediate stiffening of the mortar is required once it leaves the nozzle. To achieve such sudden structuration, liquid alumina cement or crosslinking polymer systems are applied. Moreover, in order to avoid the sag of printed mortar layers, thixotropic agents based on nanoclays including attapulgite or meta muscovite are admixed. Additionally, adhesive polymers based on synthetic latex copolymers facilitate sufficient cohesion between individual printed layers and provide the necessary form stability of the structure. Early strength development can be achieved by nucleation enhancing admixtures ("seeding materials") such as those based on C-S-H-PCE nanocomposites. The working mechanisms of those admixtures and the benefits achieved from them will be disclosed in the presentation. A major hitherto unresolved problem is excessive shrinkage of 3D printed objects. It derives from chemical shrinkage (most mortars are very high in cement content) as well as physical/dry shrinkage (the absence of formwork to protect the surface from desiccation being the main reason here). So far, no technically satisfying and economical solution in actual application (i.e. not under controlled laboratory conditions) has been found, which requires future development work. In the future, more work will be devoted to print actual concrete which should be the ultimate goal, as it by far represents the most attractive application. However, to print concrete with steel embedded currently is considered to be unfeasible. To solve this problem, completely new approaches need to be taken to devise a realistic, field-suitable method.

1. Introduction

Digital Manufacturing (often referred to as 3D printing) has become a standard process in numerous industries including the automotive [1] and airline industry [2], in utility manufacturing [3] or even in dentistry and pediatry [4]. More recently, also the construction industry has developed significant interest, and several conferences have been held on this subject [5-7]. Prominent companies which are most active in this field include Sika (Switzerland), Baumit (Austria), ApisCore (Russia), Siam Cement Group (SCG, Thailand) and WeiSun and Huashang Tengda (China).

The processes generally used in 3D construction include extrusion printing, shotcrete printing and printing in particle bed. As of today, extrusion printing has become the method of choice and by far ~ 80 % is printed based on this technology [8]. Therefore, in the following only this process will be addressed with respect to the use of chemical admixtures.

In extrusion printing, the requirements as follows exist: 1. printability: the mortar must be sufficiently fluid to allow pumping and extrusion from the nozzle. 2. structuration: immediately when dispensed from the nozzle, the mortar must develop sufficient "green strength" to maintain the shape and to not soften and subside. 3. adhesion: individual layers of mortar need to adhere well to each other in order to form a larger construct such as e.g. a wall etc. This requirement is particularly critical when printing objects with inclination. 4. acceleration: extremely fast early strength development is required in order to allow fast printing without collapse of the structure already during the printing process or shortly after completion.

In order to achieve all these properties, chemical admixtures are indispensable. Only with their help, 3D printing in construction became possible. This paper presents the key admixtures which are used in the digital manufacturing of building products, it highlights their function and correlates this with their chemical structure and mode of action.

It should be clarified that although many attempts have been made to print actual concrete including steel reinforcement, so far no one has successfully achieved this task. For this reason, the following will only address admixtures which are used in mortars applied in 3D printing, and not in concrete.

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Received 21/03/2023, explanation 25/5/2023, Accepted 11/06/2023
Link DOI: https://doi.org/10.54772/jomc.v13i01.393

2. Methods

At this moment, no industry standards exist which specifically address the requirements in 3D printing of building materials. For this reason, the methods commonly applied to test these admixtures are referenced:

Superplasticizers: DIN EN 1015-3 (spread flow) [9]

Adhesives: DIN EN 12004 (tile adhesives) [10]

Accelerators: DIN EN 196-3 (initial & final setting) [11] and DIN EN 196-1 (early strength development) [12]

Structuration: API RP 13B (10'' / 10' gel strength) [13]

3. Results and Discussion

In 3D printing, chemical admixtures and mineral additives are applied to achieve the effects as follows:

- pumpability of the ink
- providing structuration and shape stability of deposited ink
- thixotropy to avoid particle sag
- adhesion between individual deposited layers
- rapid strength development
- shrinkage control

In the following, specific products, their functionality and characteristic effects will be discussed.

3.1. PCE Superplasticizers for pumpability

Inks commonly used in digital manufacturing of building products are characterized by exceptionally high solids volume fractions and – more specific – high cement contents (350 – 480 Kg/m^3). As a result, such suspensions possess no workability and require superplasticizers to achieve pumpability. The most common kind of fluidizers includes polycarboxylate (PCE) superplasticizers (Figure 1) [14]. In Europe, the MPEG and VPEG type PCEs are most dominant whereas in Asia the HPEG and IPEG kind of PCEs are more widely used. In 3D printing, the so-called precast type of PCE (polymers of very high anionicity) provides best results because it develops maximum fluidity which quickly vanishes. A disadvantage of these polymers is that they slightly retard early strength development.

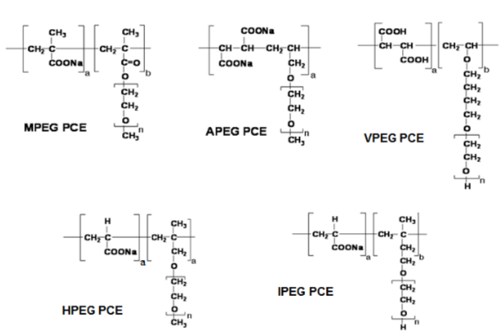

Figure 1. Chemical structures of common PCE superplasticizers.

3.2. Admixtures for structuration

Once the ink has left the nozzle, then immediate stiffening should occur in order to achieve shape stability. The most widely used product for this purpose comprises a slurry of calcium aluminate cement (CAC) which is injected just before the nozzle and results in immediate setting of the slurry [15]. The mechanism behind the prevention of CAC hydration in the aqueous slurry is adjustment of a low pH value and coating of the CAC surfaces with inorganic particles which prevents the access of water. Once this slurry is brought in contact with OPC, then the high pH activates CAC hydration and induces instantaneous set.

Another system providing immediate stiffening is based on a reaction between BNS superplasticizer and polyethylene oxide (PEO). When combined, these two polymers form a π complex (see **Figure 2**) which induces high viscosity into the slurry [16] and thus provides shape stability.

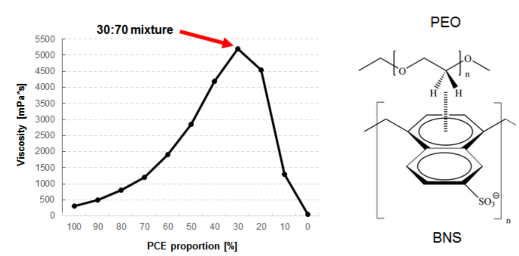

Figure 2. Formation of a π complex between BNS superplasticizer and polyethylene oxide resulting in a 10-15 fold increase of paste viscosity.

3.3. Thixotropy

Thixotropy describes the effect whereby a suspension which is fluid and exhibits low viscosity under shear becomes viscous (= stiffens) once the shear subsides. Such behavior is extremely desirable for inks which are used in 3D printing of concrete: ideally, the ink will assume a gel-like consistency once it has been extruded from the nozzle. Common thixotropic admixtures used in 3D printing are comprised of nano clays, in particular of nano-sized bentonite and attapulgite (see Figure 3). The advantage of attapulgite over bentonite is that it can provide higher thixotropy in the ion-loaded cementitious pore solution, however it requires intensive shearing to sufficiently activate the needle-like attapulgite particles to achieve this effect.

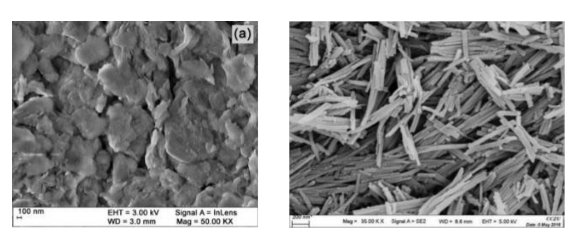

Figure 3. Morphology of platy bentonite particles (left) and of needle-like attapulgite particles (right) as observed under the scanning electron microscope [17,18].

3.4. *Admixtures for adhesion*

Individual printed layers must exhibit sufficient adhesion between each other, otherwise the entire structure may collapse shortly after printing (see **Figure 4**). To avoid such mishap, aqueous latex polymer emulsions are applied based on e.g. styrene-butadiene (SBR) or ethylene-vinylacetate (EVA) copolymer [19]. Such latex dispersions contain micro-sized polymer particles which coalesce into consistent polymer films once the water in the ink is used up by cement hydration or desiccation (see **Figure 4**). The latex dispersions can be premixed with the ink which then requires addition of a defoamer, because the emulsifiers contained in the liquid latex present strong surfactants and introduce large amounts of air.

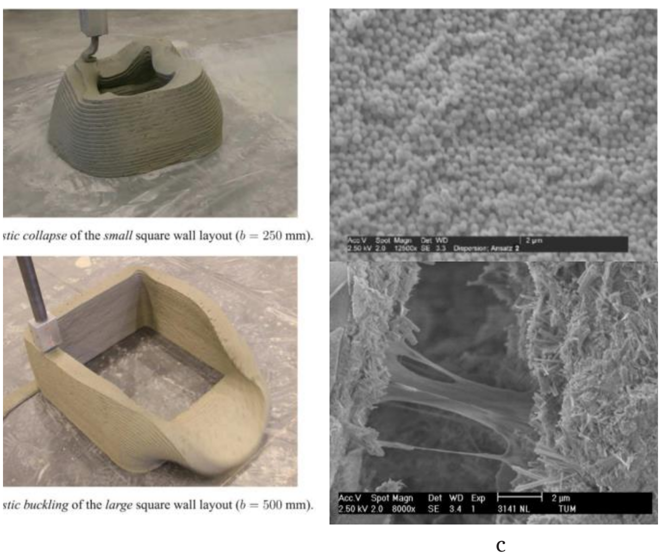

Figure 4. Example of a structure collapsed because of insufficient bonding between individual printed layers (left) [20]; SEM images of latex polymer particles before (top right) and after forming a polymer film in the mortar (bottom right).

3.5. *Rapid strength development*

The build-up of layer structures mandates that within few minutes after extrusion the ink rapidly develops sufficient early strength to support the entire object. Ideally, once printed the ink should exhibit a right angle set and immediately transgress into the hardening stage. In order to achieve this, hardening accelerators are applied. Depending on the effect required, common shotcrete accelerators including calcium formate, sodium silicate, sodium aluminate or aluminum hydroxy sulfate are admixed [21]. Their effectiveness relies on instantaneously induced crystallization of cement hydrates. However, owed to this flash precipitation, the hydrate crystals are of poor quality and less densely packed. As such, inspite of the early strength achieved, a much reduced (~ 50 %) final strength is observed which is sometimes undesirable.

A viable alternative accelerator is presented by nano-sized calcium silicate hydrate-polycarboxylate (C-S-H-PCE) seeding materials (see **Figure 5**). These composites consist of particularly small C-S-H foils (l < 100 nm) which act as seeding material for C-S-H formation by providing C-S-H clusters of sufficient size (> critical cluster size), thus avoiding the delaying step of initial cluster formation [22]. Through this mechanism, relatively high early strength values already after ~ 5 hours are attainable, at no sacrifice in final strength. For this reason, C-S-H-PCE nanocomposites have found large-scale application in cementitious systems such as e.g. floor screeds where high early strength is required.

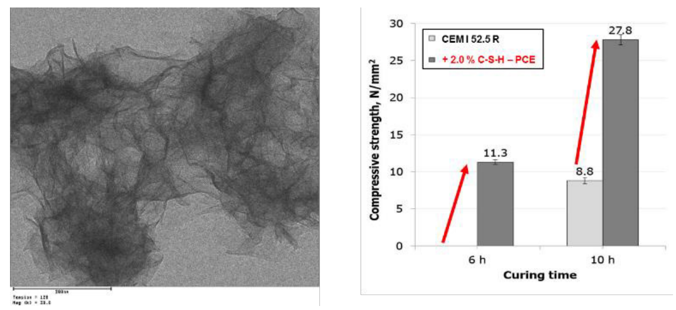

Figure 5. Foil-like nano-sized C-S-H-PCE accelerator (left, TEM image) and accelerating effect of such nanocomposites on early strength development of a cement mortar (right).

3.6. *Shrinkage control*

Shrinkage still presents a major problem in digital manufacturing of cement-based materials. First, because of the elevated cement contents commonly used in the inks, autogeneous shrinkage is considerable. Second, as there is no formwork which protects the structure from desiccation by wind and sun, dry shrinkage is substantial.

To overcome the problems of dry shrinkage, common shrinkage reducing admixtures which are usually based on diols, glycols or polyols are added to the ink (**Figure 6**). Yet in order to be effective, relatively high dosages of these alcohols (~ 2 - 3 % by weight of cement) need to be applied and the effect still often is not as desired. Even more difficult to solve is the problem of autogeneous shrinkage. Here, shrinkage compensators such as monocalcium aluminate (CA) which works via C-A-H formation or entirely shrinkage compensated binder systems (e.g. based on a ternary binder system of OPC/CAC and anhydrite) have been evaluated, yet results were mixed. The problems encountered were difficulty to determine the correct dosage of CA and to accelerate setting in the ternary binder system. As a consequence, no practical solution exists as of today which can guarantee proper control of both autogeneous (chemical) and dry (physical) shrinkage.

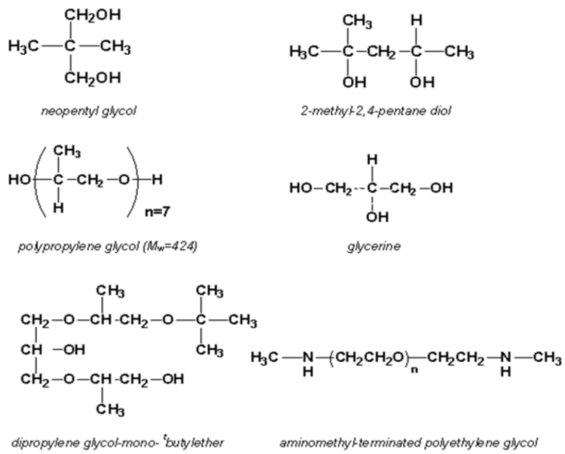

Figure 6. Selection of shrinkage-reducing admixtures commonly used in cement-based building materials to control dry shrinkage.

4. Conclusion

Compared to other industries, digital manufacturing in the construction industry still is at an early, premature stage and faced with numerous problems. Above all it has been recognized and is generally accepted now that, next to the printing hardware, admixtures play a pivotal role to achieve the properties which are indispensable for successfully building up larger structures. At the moment, much euphoria exists which – according to the famous “Gartner hype cycle” [23] – presents the peak of inflated expectations. The reality at present however is that in construction, so far all inks are based on mortar only which limits the objects to be printed to decorative products such as vases, shelters, tables, chairs, etc. Whereas, the main benefit from this technology would lie in the manufacturing of large concrete structures including multi-story homes, pillars, bridges and other objects of infrastructure. However, at the moment the simultaneous printing of steel reinforcement and concrete appears to be impossible and no concept is on the horizon which allows optimism in this direction. As such, the industry is focusing its efforts now more e.g. on printing formwork for larger concrete structures and other objects which do not require steel reinforcement.

Only future can tell how much inroad into the construction industry digital manufacturing will make, yet it is safe to assume that chemical admixtures will present a most critical key technology for the success in this sector.

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