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Rheological and mechanical properties of admixtures modified 3D printing sulphoaluminate cementitious materials

Mingxu Chen [a,b], Laibo Li [a,b], Yan Zheng [a], Piqi Zhao [a,b], Lingchao Lu [a,b,*], Xin Cheng [a,b,*]

[a] School of Materials Science and Engineering, University of Jinan, Jinan 250022, China
[b] Shandong Provincial Key Lab. of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, China

HIGHLIGHTS

- Rheological behaviors of 3D printing cementitious materials were investigated.
- RSM was adopted to clarify the effect of hybrid admixtures in 3D printing paste.
- The control range of viscosity and yield stress for 3D printing was first suggested.

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ABSTRACT

3D printing for cement-based material is recently supposed to be the rapidly and innovative forming technology in the building industry. This paper is concentrated on the rheological and mechanical properties of hydroxypropyl methyl cellulose (HPMC), water-reducing agent (WRA) and lithium carbonate (Li_2CO_3) modified 3D printing sulphoaluminate cementitious materials based on the extrusion system of 3D printing. Experimental results show that HPMC notably increases the stress and viscosity of cement paste and the plastic viscosity need to reach 1.650 ~ 2.538 Pa·s for the build-up of 3D structures. While the cement paste with WRA and Li_2CO_3 present low shear stress and apparent viscosity. Furthermore, the setting time and rheological properties of 3D printing cement paste with hybrid admixtures are investigated using response surface methodology (RSM). The optimal hybrid additions of admixtures enable the 3D printing paste to achieve a favorable deformation rate and higher compressive strength. In conclusion, utilization of admixtures has a great potential to develop 3D printing sulphoaluminate cementitious materials used in buildings, which can effectively control the printable properties and rheological behaviors.

1. Introduction

3D printing is an advanced and green manufacturing technology to build the structure based on the model of layer by layer, which has been developed successfully in the area of metal materials, advanced ceramics, polymeric materials, etc [1–3]. 3D printing for cement-based material is recently supposed to be the rapidly and innovative forming technology in the building industry. Besides, modern and archaistic buildings require a large number of 3D printed cement-based functional components with complex structure and special-shaped [4,5]. Compared with the traditional cement-based materials, 3D printing is based on the digital and three-dimensional model and printed through the manner of layer by layer in the printer nozzle to build the complex building structures [6]. However, cement-based materials for 3D printing present some problems, such as long setting time, low early strength and easy cracking [7].

3D printing requires the cement-based materials to present the behavior of well-flowing and easy-extrusive when the paste in the delivery system [8,9]. Furthermore, the printed cement-based materials should be well-buildable and high-cohesiveness in order to reach a continuous paste from the printing nozzle and ensure a rapidly hardening structure [10,11]. Le et al. [12,13] proposed three basic requirements for 3D printing cement-based materials: (1) the materials can be extruded from the printing nozzle to ensure the flowability and extrudability; (2) the materials should have good cohesiveness so that it printed continuously; (3) the materials should present short setting time and high early strength. Nevertheless, the cementitious materials and its mix proportion is very difficult to handle these behaviors, therefore admixtures are

* Corresponding authors at: School of Materials Science and Engineering, University of Jinan, Jinan 250022, China.
E-mail address: lingchao_lu@163.com (L. Lu).

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necessary for 3D printing cement paste to improve the buildability, printability and early strength [14].

Some researches have been conducted to investigate the printability and mechanical strength of 3D printing cement-based materials. Hambach et al. [15] investigated the properties of 3D printing fiber-reinforced Portland cement paste, and they found that effective fiber alignment would lead to a remarkable increase of flexural strength of the composites and the alignment of the fibers along with the print path direction. Ma et al. [16] researched the printable properties of cementitious material containing copper tailings for based on 3D printing extrusion system, finding that the optimal mixture was determined as substituting natural sand with 30% mass ratio of mining tailings, which enabled structures achieve a favorable buildability and a relatively high mechanical strength. Besides, the bonding strength is also important for the structure build-up of 3D printing cement-based materials. Zareiyan et al. [17] studied the effects of interlocking on interlayer strength of structures in 3D printed concrete and indicated that bonding strengths is sensitive to interlocking and it can be increased by an average of 26% based on the appropriate concrete mixtures. However, there is little research about 3D printing has been done on the sulphoaluminate cement. Sulphoaluminate cement exhibits two desirable features, high early strength and fast hardening, which are in favor of the build-up of 3D structures and provided the high early mechanical properties [18].

Rheology is the science of flow and deformation of matter, which investigates the relationship between stress, shear rate and time [19]. Hence, theology is an important evaluation parameter to characterize the deformation and workability of fresh paste, and predict the flow behavior, print status of 3D printing cement paste, which will affect the mechanical strength, the build-up of structures, and engineering applications [20].

However, the research for the rheology of 3D printing cement paste is limited by the involved admixtures. In this paper, hydroxypropylmethyl cellulose (HPMC), water-reducing agent (WRA) and lithium carbonate (Li_2CO_3) were used to control the printability and improve the mechanical strength of 3D printing sulphoaluminate cement paste, and a systematic investigation on rheology was carried out to clarify the variation of stress and viscosity for 3D printing sulphoaluminate cement paste. Besides, response surface methodology (RSM) was adopted to optimize the hybrid addition of admixtures in the 3D printing sulphoaluminate cement-based materials.

2. Materials and methods

2.1. Raw materials and procedures

Sulphoaluminate cement (42.5 grade, Qufu zhonglian company, CHN) serves as the main cementitious materials to improve the setting time and early strength. The chemical components of sulphoaluminate cement were shown in Table 1. Hydroxypropyl methyl cellulose (HPMC, 200000 mPa·s, CHN) and water reducing agent (WRA, polycarboxylate, CHN) with a water reducing rate of 32% were used to improve the flowability and buildability by controlling the viscosity and stress of paste. Lithium carbonate (Li_2CO_3, CHN) was adopted to promote the cement hydration and shorten the setting time.

The flow chart of the fabrication and characterization of the 3D printing cement-based materials is shown in Fig. 1 and detailed preparation procedures are as follows:

1) Sulphoaluminate cement was firstly blended with HPMC for 2 h to obtain a uniform mixture through the V-shape blender mixer;
2) WRA and Li_2CO_3 were mixed with the above mixture at the water to cement (w/c) ratio of 0.35 and stirred for 3 min;
3) The fresh mixture was put into the charging barrel and shaken evenly, and then it was installed to 3D printer to print samples;
4) Printed samples was cured at 20 °C for 24 ~ 72 h in a relative humidity of 95%.

2.2. 3D printing system

Fig. 2 exhibits the structural schematic diagram of 3D printing machine used for the build-up of 3D cement paste structures. In general, 3D printing system comprises of sliding axle, extrusion device, charging barrel, platform and LCD operator panel. The size of this machine is 0.88 m (length) * 1.04 m (width) * 1.08 m (height) and the printing speed was set as 15 mm/s.

2.3. Test methods

2.3.1. Setting time

GB-T 1346-2011 [21] was followed and a manual Vicat apparatus was used to determine the initial and final setting time of 3D printing cement pastes and the penetration of the Vicat needle into cement paste at 36 ± 1 mm and 0 mm were determined as the initial and final setting time.

2.3.2. Hydration heat evolution

A conduction calorimeter (TAM Air C80, Thermometric, Sweden) operating at 25 °C was used to measure the hydration heat flow and cumulate heat. In this purpose, the w/c ratio was set as 0.35, the heat flow and cumulate heat was recorded every 44 s until 24 h.

2.3.3. Deformation rate

The deformation rate was measured according to the deformation degree of length, width and height for 3D printing samples (Fig. 3(a)) and obtained by referring to the positive strain. The deformation rate of a sample was calculated as:

$$D = [(l - l_0)/3l_0 + (d - d_0)/3d_0 + (h_0 - h)/3h_0] * 100\%$$

where D is the deformation rate, l_0, d_0, and h_0 represent the size of model, l, d, h represent the size of samples after printing.

2.3.4. Rheology

Rheology is the science of flow and deformation of matter, and investigates the relationship between stress, shear rate and time. Compared with traditional cement-based materials, the requirement of viscosity and stress for 3D printing is different (Fig. 3(b)), it exhibits that the materials present low yield stress and well-flowability from the charging barrel to printer nozzle and the fresh paste after printing should get high viscosity and short setting time. In this paper, the test program is shown in Fig. 4(a), 0 ~ 2 min is the premix stage for uniform distribution of slurry and then rest for two minutes. Thereafter, the shear rate increases from 0 to 200 s^{-1} in 4 ~ 6 min and decreases from 200 to 0 s^{-1} in 6 ~ 8 min. The rheometer automatically record shear rate, shear stress, apparent viscosity in the process of testing. Bingham equation is adopted to obtain the yield stress and plastic viscosity, Fig. 4(b) shows the plastic viscosity and yield stress obtained from linear fitting curve for shear rate-stress curve (stable stage of 50 ~ 150 s^{-1}) based on Bingham model. The plastic viscosity presents the difficulty level of the destruction for colloidal system when the cement paste is at rest and the yield stress means the minimum force required for the flow of the paste. These two factors may play important roles in the build-up of 3D structures.

2.3.5. Mechanical properties

Mechanical properties of 3D printing samples cured 1 d were tested by using a universal testing machine (MTS) at a loading speed of 0.3 KN/s and measuring range of 10 ~ 300 KN.

Table 1
The chemical components of sulphoaluminate cement (% by mass).

CaO	Al_2O_3	SO_3	SiO_2	Fe_2O_3	TiO_2	K_2O	MgO	Others	Loss on ignition
49.50	20.17	14.91	8.51	1.97	1.57	0.90	0.77	0.73	0.97