



Magneto-rheology control in 3D concrete printing: A rheological attempt

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ARTICLE INFO

Keywords:

Active rheology control
Cement paste
3D concrete printing
Magnetic field

ABSTRACT

The application of magneto-rheology control in extrusion-based 3D concrete printing is conceptually examined by rheological experiments on cementitious paste with nano-Fe₃O₄. The extruding process is simulated by a constant shearing, and the buildability after extrusion is characterized by the structural build-up from small amplitude oscillatory time-sweep test. A pulsed magnetic field is applied during shearing and then removed when the shearing terminates. It is revealed that some residual magnetic clusters exist in the suspension after removing the magnetic field due to the remanent magnetization of the nanoparticles. This results in a faster structural build-up compared to the situation without being treated by magnetic field, and this is independent of the magnetic field duration within the considered range from 1 s to 5 s. This finding offers an innovative methodology to actively improve the buildability of 3D printed concrete by introducing a short-pulsed magnetic field during extrusion.

1. Introduction

3D printing of concrete needs to meet contradicting requirements regarding pumpability, extrudability, and buildability [1,2]. On the one hand, the material needs to flow easily to be pumped towards the printing unit and to be extruded through the nozzle. On the other hand, after the printed material reaches its final position in the printed layers, the yield stress of the mixture should be high enough to maintain its shape under its own weight and the load from upper layers [3–5]. In current practice, it is not straightforward to obtain a good balance between flowability and buildability for the same concrete mixture. Active control of structural build-up is a potential solution to overcome this challenge.

This current research examines the potential application of magneto-rheology control in extrusion-based 3D concrete printing by rheological experiments on cementitious paste with nano-Fe₃O₄ particles. The extruding process is simulated by constant shearing, and the buildability after extrusion is characterized by structural build-up using oscillatory time sweep test. A short-pulsed magnetic field is applied to the cementitious paste at the end of the shearing. The subsequent evolution of storage modulus, regarded as a post-effect of the applied magnetic field, is evaluated and correlated to the duration of the magnetic field and the magnetic properties of the nanoparticles.

2. Experimental program

2.1. Materials and sample preparation

CEM I 52.5N Portland cement (OPC) and two spherical nano-Fe₃O₄ particles (designated as MNP1 and MNP2, from US Research Nanomaterials, Inc.) were used. The chemical composition and physical properties of the cement and nanoparticles are shown in Table 1. De-ionized water was utilized.

Cementitious pastes with water-to-cement (w/c) ratio of 0.45 and nano-Fe₃O₄ content of 3% (by mass of cement + water) were prepared. The pastes have excellent stability and appropriate flowability after mixing. The cementitious pastes were mixed using a rotational rheometer equipped with a helix geometry [6]. After adjusting the helix rotator to the mixing position, the rotational speed increased linearly from 0 to 3000 rpm within 30 s and then continuously mixed at this speed for another 120 s.

2.2. Rheological testing protocol

The rheological test for examining the structural evolution of cementitious paste is performed by using a parallel plate rotational rheometer (MCR 102, Anton Paar) equipped with magneto-rheological

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<https://doi.org/10.1016/j.matlet.2021.131374>

Received 15 October 2021; Received in revised form 16 November 2021; Accepted 22 November 2021

Available online 26 November 2021

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Table 1Chemical composition and physical properties of cement and nano-Fe₃O₄ particles.

Chemical composition of Portland cement						
Components	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
wt. %	19.4	6.04	4.12	61.5	1.25	5.35
Physical properties						
	OPC	MNP1	MNP2			
Specific gravity	3.20	4.95	4.95			
Average particle size*	7.199 μ m	100 nm	200 nm			
Saturation magnetization	0.59 Am ² /kg	77.29 Am ² /kg	77.56 Am ² /kg			
Remanent magnetization	0.05 Am ² /kg	14.81 Am ² /kg	10.23 Am ² /kg			

*The average particle size of the nano-Fe₃O₄ particles is supplied by the manufacturer.

device (MRD). The diameter of the plate is 20 mm, and the gap between the parallel plates is fixed at 1 mm. The rheological protocol simulating 3D concrete printing is presented in Fig. 1. Extrusion-based 3D concrete printing process includes mixing, pumping, and extruding. From the viewpoint of rheological measurements, a pre-shearing with a shear rate of 100 s⁻¹ for 30 s is used to simulate the mixing process. The pumping and extruding processes are simulated by a constant shearing with a relatively low shear rate of 20 s⁻¹ for 60 s. The structuration of the paste after extrusion is described by the structural build-up obtained from oscillatory time sweep test, where the shear strain and frequency were fixed at 0.005% (within the linear viscoelastic region) and 2 Hz, respectively. For the normal 3D printing simulation, no magnetic field is applied. For the magneto-controlled 3D printing, a pulsed magnetic field (PMF) is applied towards the end of the shearing, lasting for 1 s or 5 s. The removal of the PMF occurs simultaneously with the termination of the shearing. During the rheological test, the temperature was maintained at 20 \pm 0.5 $^{\circ}$ C, and the data was recorded every second.

3. Results and discussion

Fig. 2 presents a typical evolution of shear stress and storage modulus of cementitious paste containing MNP1. For the situation without PMF, the storage modulus increases linearly from \sim 50 kPa after terminating the shearing. This indicates the gradual increase of the internal structuration of the paste. If a 1s-PMF is applied towards the end of shearing, the shear stress immediately jumps to a high value. When the shearing terminates and the 1s-PMF is removed, the microstructure starts to build up at a relatively higher initial strength. Indeed, the storage modulus shows a significant increase within the first ten seconds with an initial value higher than 100 kPa. With elapsing resting time, the storage modulus gradually increases with a higher growth rate than the case without applied PMF. The results indicate that the application of a PMF during extrusion in 3D printing will possibly lead to a higher evolution of structuration of cementitious paste with magnetic particles. Fig. 2 also shows that the faster structural build-up after extrusion is independent of the duration of the PMF, within the range considered here.

The results can be explained by the distribution of magnetic nanoparticles. It is postulated that the nanoparticles are randomly distributed in the voids between cement particles during shearing, as shown in schematic diagram (a) in Fig. 2. When applying a magnetic field, the

nanoparticles agglomerate to chains/clusters in a very short time [7–9], as depicted in diagram (b) in Fig. 2. Furthermore, the flowing paste tends to facilitate the formation of magnetic chains/clusters [10]. This exerts a resistance to the shear flow, resulting in a jump increase in the shear stress. Note that the possible negative influence of the jumped shear stress to extrudability could be neglected due to the very short magnetic field. After removal of the magnetic field, the formed magnetic clusters are disassembled, while some residual chains/clusters remain in the suspension, as presented in diagram (c) in Fig. 2, due to the intrinsic properties of the nanoparticles (i.e., high remanent magnetization (14.81 Am²/kg) of MNP1 in Table 1). The presence of the residual clusters, on the one side, results in an initial microstructural strength of the cementitious paste, and thus a relatively high initial storage modulus is observed. On the other side, the residual clusters enhance the interactions between solid particles, improving the structural evolution of the cementitious paste.

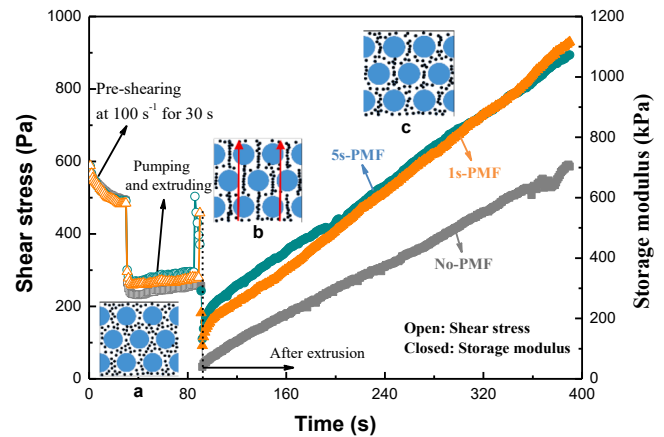


Fig. 2. Typical evolution of shear stress and storage modulus of cementitious paste (w/c = 0.45, 3% MNP1).

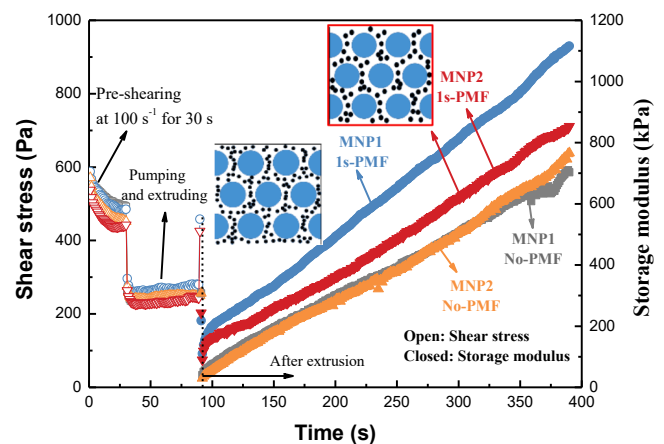


Fig. 3. Effect of nano-Fe₃O₄ type on the magneto-induced structural build-up of cementitious paste (w/c = 0.45, 3% nano-Fe₃O₄).

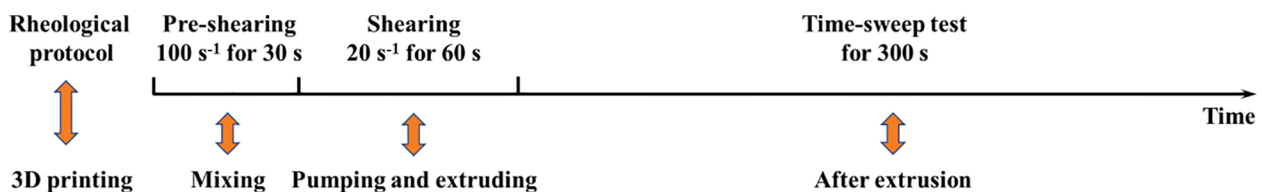


Fig. 1. Rheological testing protocol simulating extrusion-based 3D concrete printing.

In order to validate the proposed hypothesis, the PMF-induced structural build-up of two cementitious pastes containing two different types of nano-Fe₃O₄ particles with same saturation magnetization but different remanent magnetization and particle size was compared, as shown in Fig. 3. Without magnetic field, the two mixtures have almost similar evolutions of storage modulus. This is consistent with our previous findings [11], which shows that changing the particle size of nano-Fe₃O₄ has negligible influence on the structural evolution without magnetic field. According to the proposed hypothesis, if applying a PMF, the increase of shear stress for the two mixtures should be similar in the magnitude due to the same saturation magnetization. After removing the PMF, less residual magnetic clusters should exist in the MNP2-paste compared to the MNP1-paste because of the relatively lower remanent magnetization of MNP2 than MNP1. Therefore, MNP1-paste should exhibit faster structural build-up than that of MNP2-paste in the subsequent resting period. It can be observed from Fig. 3 that all the experimental results are consistent with the expectations.

Overall, applying a PMF during extruding seems to be a potential method to actively improve the stiffness of cementitious materials after extrusion, thanks to the intrinsic properties (i.e., high remanent magnetization) of magnetic particles. Nevertheless, further research regarding magneto-rheology control in real 3D concrete printing is required, including apparatus set-up and materials design.

4. Conclusions

The potential of magneto-rheology control in extrusion-based 3D concrete printing is conceptually examined by rheological experiments. It is found that cementitious paste with nano-Fe₃O₄ particles shows higher structural build-up after removing the pulsed magnetic field which is applied before the time sweep test. The result is independent of the magnetic field duration. This is correlated to possible residual magnetic clusters formed under magnetic field because of the presence of remanent magnetization characteristic of the nanoparticles. The findings clear the path to actively improve the buildability of cementitious materials for 3D printing by introducing a short-pulsed magnetic field during extrusion. Further research regarding nozzle and materials design for magneto-rheology control of 3D concrete printing is ongoing.

CRedit authorship contribution statement

Dengwu Jiao: Methodology, Conceptualization, Investigation, Formal analysis, Writing – original draft. **Caijun Shi:** Writing – review & editing, Supervision. **Geert De Schutter:** Supervision, Writing – review

& editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The financial support from the European Research Council (ERC) Advanced Grant project ‘SmartCast’ (693755) is gratefully acknowledged.

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