Structural evolution of cement paste with nano-Fe$_3$O$_4$ under magnetic field - Effect of concentration and particle size of nano-Fe$_3$O$_4$

Dengwu Jiao [a,b], Karel Lesage [a], Mert Yucel Yardimci [a], Khadija El Cheikh [a], Caijun Shi [b], Geert De Schutter [a,*]

[a] *Magnel-Vandepitte Laboratory, Department of Structural Engineering and Building Materials, Faculty of Engineering and Architecture, Ghent University, 9052, Ghent, Belgium*
[b] *Key Laboratory for Green and Advanced Civil Engineering Materials and Application Technology of Hunan Province, College of Civil Engineering, Hunan University, Changsha, 410082, China*

ABSTRACT

The effects of concentration and particle size of nano-Fe$_3$O$_4$ particles on the evolution of structural build-up of cementitious paste under magnetic field are experimentally investigated and then verified by theoretical calculations. Three types of nano-Fe$_3$O$_4$ particles with various particle sizes are exploited. The results show that the liquid-like properties of the nano-Fe$_3$O$_4$ incorporated cementitious pastes increase immediately after initiation of an external magnetic field and the extent of this increment increases with the nano-Fe$_3$O$_4$ content. The magneto-rheological effect, quantified by the difference of the storage modulus at 300 s between 0 T and 0.5 T, increases with increasing concentration of the nanoparticles. The particle size of nano-Fe$_3$O$_4$ particles plays a dominant role in the viscoelastic properties without magnetic field, whereas the rheological response of the cementitious paste to an external magnetic field is mainly determined by the crystalline structures and magnetic properties of the nano-Fe$_3$O$_4$ particles. The magnetic yield parameter is a useful indicator to describe the intensity of the magneto-rheological response, and the increase rate of the loss modulus at early age is proportional to the movement velocity of the nano-Fe$_3$O$_4$ particles.

1. Introduction

SmartCast [1–3], including active rheology control (ARC) and active stiffening control (ASC), is a ground-breaking concept aiming at achieving smart and controlled casting operations in cement-based materials. Available property control methods follow the principle that according to the relationships between properties and mixture proportions, the desired concrete properties are achieved by pre-adding appropriate mineral additives or chemical admixtures [4,5]. The properties of prepared concrete mixtures, however, cannot be further controlled during casting processes. In this context, the active control proposed in SmartCast provides an adjustment scheme in post-mixing properties of cement-based materials. By activating an external trigger signal, the rheological properties of fresh cementitious materials with responsive particles can be artificially controlled. This concept is beneficial for eliminating the contradictions in requirements of fresh concrete performances in different operation processes, such as the contradicting requirements in structuration rate during pumping and

formwork casting processes [6–8].

A potential approach to achieve active rheology control is adding magnetic particles in combination with exploiting an external magnetic field [2,9]. The controllable rheology of cementitious materials by applying a magnetic field is based on the theoretical foundations of magnetorheological (MR) fluids. MR fluids are considered as smart materials with magnetic particles dispersed in a carrier fluid. In the absence of a magnetic field, the magnetic particles distribute randomly in the carrier fluid and the MR fluid approximately exhibits Newtonian behavior. After applying an external magnetic field, the magnetic particles are promoted to align to form chain- or column-like structures. The MR fluid transforms from liquid to semi-solid state within milliseconds, with viscosity increasing about 10^5–10^6 times and field-induced yield stress increasing up to 100 kPa [10]. When the external magnetic field is removed, the magnetic particles are demagnetized and the MR fluid reversibly changes from semi-solid to liquid state. Therefore, the controllable MR fluids are broadly applied in many practical applications such as dampers, brakes, polishing, medical devices, etc. [11,12].

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* Corresponding author.
E-mail address: geert.deschutter@ugent.be (G. De Schutter).

With regard to cement-based materials, an external magnetic field can be easily applied during a construction process, and thus could be a potential approach to alter or control the properties. The properties of lubrication layer and thus the pumpability of fresh concrete seem to be somewhat increased by applying an electromagnetic field [13]. Applying an external magnetic field has been shown as a solution to control the orientation of steel fibers and improve the compaction properties of concrete [14]. Besides, fresh cement pastes exposed to an external magnetic field have larger amount of C-S-H gel, denser morphology and less porosity [15]. In the context of rheology control on-demand, Nair and Ferron [16,17] found that the rheological properties of fresh cement paste containing carbonyl iron particles can be significantly altered by applying an external magnetic field.

Nano-Fe_3O_4 particles have attracted extensive attention in cement-based materials. The cementitious materials containing nano-Fe_3O_4 particles generally exhibit increased mechanical properties, excellent electromagnetic wave absorption properties, and enhanced resistance to water absorption and chloride penetration [18,19]. In view of active rheology control of cementitious materials, nano-Fe_3O_4 particles can be added as the responsive particles. The structural build-up of cementitious paste with magnetic nano-Fe_3O_4 particles is presented in Refs. [20, 21]. Results show that the cementitious paste exhibits totally liquid-like behavior immediately after applying an external magnetic field due to the mechanical micro-agitation effect of the moving nanoparticles. With the increase of magnetization duration, the stiffness of the cementitious paste is enhanced because of the formation of magnetic clusters. Higher clustering of nano-Fe_3O_4 particles corresponds to more obvious magneto-rheological responses [22]. Moreover, the evolution of visco-elastic properties of cementitious paste with nano-Fe_3O_4 particles is apparently controlled by the application mode of time-varying magnetic field [23].

Recently, the magnetic force and movement velocity of nanoparticles in cementitious suspensions under external magnetic field were derived [24,25]. Assuming that all magnetic nanoparticles have same constant dipole moments and are arranged in the voids between cement particles as simple cubic order with same inter-particle distance, the competition between the magnetic force of two neighboring nanoparticles with center line along the direction of the magnetic field and the resistance force caused by the viscoelastic stress of the cementitious suspension can be characterized by magnetic yield parameter (Y_M^*):

$$Y_M^* = \frac{\mu_0(\rho M)^2}{24\tau_{c,ys}}\left(\frac{6\varphi_{MNPs}}{\pi}\right)^{\frac{4}{3}} \tag{1}$$

where μ_0 is the magnetic permeability of the medium (assumed to be the value of vacuum, $4\pi \times 10^{-7}$ N/A^2), ρ and M are the density (kg/m^3) and the magnetization per unit mass (Am^2/kg) of the nanoparticles, respectively. $\tau_{c,ys}$ is the elastic limit yield stress (Pa), corresponding to the intensity of C-S-H bridges between cement grains [24,25]. φ_{MNPs} is the volume fraction of the nanoparticles relative to the voids between cement particles, which can be calculated as:

$$\varphi_{MNPs} = \frac{V_{MNPs}}{(1 - \varphi_C) \cdot V_{Total}} \tag{2}$$

where φ_C is the volume fraction of cement particles (%), V_{MNPs} and V_{total} are the volume of nanoparticles and total suspensions (kg/m^3), respectively. The magnetic yield parameter is a representative indicator to describe the possibility of nanoparticles movement at the beginning of applying an external magnetic field. When $Y_M^* > 1$, the magnetic force overcomes the resistance of the suspension and magnetic chains or clusters can be formed. The sample will show a significant magneto-rheological response. However, $Y_M^* < 1$ means that the suspension prevents the structure formation of chains or clusters. In the case of $Y_M^* > 1$, the cementitious paste is considered to exhibit slight flow behavior due to the micro-agitation effect of the moving nanoparticles. Assuming an equilibrium between magnetic force and viscous drag force while moving through the interstitial medium, the theoretical equilibrium velocity of the nanoparticles can be equated by:

$$v = \frac{d}{\mu_{pl}}\left[\frac{\mu_0(\rho M)^2}{72} \cdot \left(\frac{6\phi_{MNPs}}{\pi}\right)^{\frac{4}{3}} - \tau_{pl}\right] \tag{3}$$

where v is the movement velocity of nanoparticles (m/s), τ_{pl} and μ_{pl} are the Bingham yield stress (Pa) and plastic viscosity (Pa.s) of the suspension, respectively, and d is the average particle size of the nanoparticles (m). For consistency with zero velocity in the case of $Y_M^* = 1$, the term τ_{pl} is replaced by one third of the elastic limit yield stress, and μ_{pl} is selected as the plastic viscosity of the suspension at linear low shear rate region [25]. From Eqs. (1) and (3), it can be clearly seen that the magnitude of the magnetic yield parameter depends on the concentration and physical nature of the nanoparticles and the viscoelastic properties of the suspension. For the movement velocity of nanoparticles under a magnetic field, the particle size of the nanoparticles also plays a significant role.

In the current study, the influences of concentration and particle size of nano-Fe_3O_4 particles on the evolution of structural build-up of cementitious paste are first experimentally investigated. Three types of nano-Fe_3O_4 particles with various particle sizes are utilized. Afterwards, the magnetic yield parameter and theoretical movement velocity of the nano-Fe_3O_4 particles for each suspension under specific magnetic field are calculated. The relationships between the theoretically calculated parameters and the measured rheological parameters are tentatively established. This research provides a fundamental understanding on the magneto-rheological properties of cementitious materials concerning the concentration, particle size and magnetic properties of nano-Fe_3O_4 particles.

2. Experimental program

2.1. Materials

CEM I 42.5 N Portland cement (OPC) conforming to EN 196–1 [26] is used in this study. The chemical composition and particle size distribution are respectively shown in Table 1 and Fig. 1. The specific gravity and specific surface area (Blaine) are 3.15 and 279.5 m^2/kg, respectively. Three types of spherical Iron Oxide Fe_3O_4 particles (US Research Nanomaterials, Inc) with different grain sizes (i.e. 20-30 nm (MNP1), 100 nm (MNP2) and 200 nm (MNP3)), supplied by the manufacturer, are used. The specific gravity of the nano-Fe_3O_4 particles is 4.95. The magnetic properties of the nano-Fe_3O_4 particles and cement particles are measured by a vibrating sample magnetometer (VSM) at 25 °C. The curves of magnetization versus magnetic field strength are shown in Fig. 2, and the main magnetic parameters of the raw materials are summarized in Table 2. The crystal structure of the nano-Fe_3O_4 particles is analyzed by an X-ray diffraction (XRD) device with CuKα radiation at room temperature. Scans were recorded with scanning range (2θ) from 20° to 70° and scanning speed of 2°/min. The XRD patterns of the nano-Fe_3O_4 particles are presented in Fig. 3. De-ionized water is used to prepare all samples.

Table 1
Chemical composition of Portland cement.

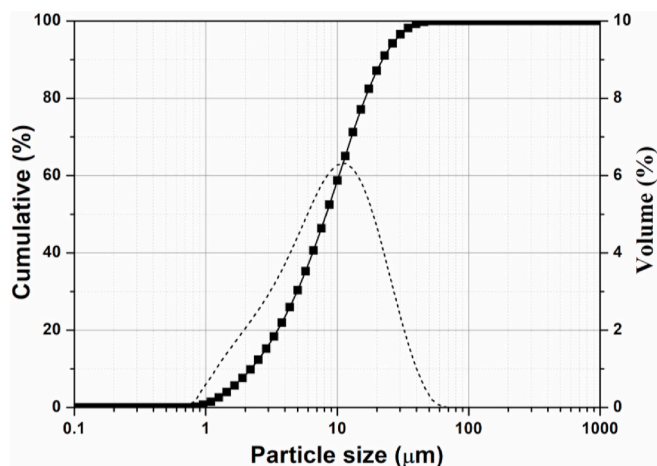| Components	% by mass
SiO$_2$	19.6
Al$_2$O$_3$	4.88
Fe$_2$O$_3$	3.14
CaO	63.2
MgO	1.8
SO$_3$	2.9

Fig. 1. Particle size distribution of the Portland cement.

2.2. Sample preparation

The water-to-cement ratio (w/c) of the cement paste medium is fixed at 0.4. The contents of nano-Fe$_3$O$_4$ particles are selected as 0%, 0.25%, 0.5%, 1%, 2% and 3% by the mass of total cement paste (i.e. cement + water). Prior to introduction, the nanoparticles have not been specially treated. All samples are prepared using a rheometer (MCR 52, Anton Paar) with a helix-shaped rotator. The geometric parameters of the helix geometry and the mixing procedure can be found in Ref. [23]. This mixer and corresponding mixing procedure with high rotational speed of 3000 r/min provide repeatable initial state of paste samples for the same mixture proportion.

2.3. Testing methods

A rotational parallel plate rheometer (MCR 102, Anton Paar) with magneto-rheological device (MRD) is used to determine the rheological properties of cementitious paste. The effective diameter of the plate is 20 mm and the gap between the upper and lower plates is fixed at 1 mm. A homogeneous magnetic field perpendicular to the plates can be applied to the sample by inputting specific electric current. During the rheological tests, the temperature of all samples is controlled at 20 ± 0.5 °C. For each mixture proportion, rheological tests are repeated three times using fresh samples.

The testing protocol for evaluating the structural build-up of cement paste is presented in Fig. 4. The magnetic field is applied to the sample at the beginning of the oscillatory time sweep test and the magnetic field strength used in this study includes 0 T and 0.5 T. The oscillatory strain

sweep test at the second step is used to obtain the linear viscoelastic region (LVER) and the elastic limit yield stress of cementitious paste without external magnetic field. During the strain sweep test, the shear strain sweeps logarithmically from 0.0001% to 10% at constant frequency of 2 Hz. The strain amplitude and frequency during the time sweep test are 0.001% and 2 Hz, respectively. A representative strain sweep testing result is displayed in Fig. 5. At relatively low shear strain, the storage modulus shows a plateau, and at shear strain higher than a critical strain, the storage modulus starts to decline, indicating the breakage of C-S-H links between cement particles [27]. The critical strain can be determined by the point where the storage modulus deviates 10% from the plateau [28,29]. The elastic stress at the critical strain is defined as the elastic limit yield stress, which can be calculated as:

Table 2
Magnetic properties of the used cement and nano-Fe$_3$O$_4$ particles.

Materials	Saturation magnetization (Ms, Am^2/kg)	Remnant magnetization (Mr[a], Am^2/kg)	Coercive field (Hc[b], Oe)
Cement	0.59	0.05	70.72
MNP1	49.48	5.13	48.88
MNP2	77.29	14.81	134.01
MNP3	77.56	10.23	108.27

[a] Mr is the magnetization left behind in a material after an external magnetic field is removed.

[b] Hc is the ability of a material to withstand a magnetic field without becoming demagnetized.
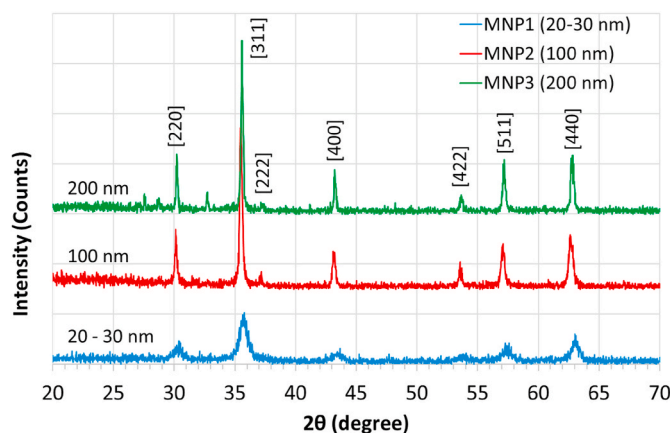

Fig. 3. XRD patterns of the nano-Fe$_3$O$_4$ particles with different particle sizes.
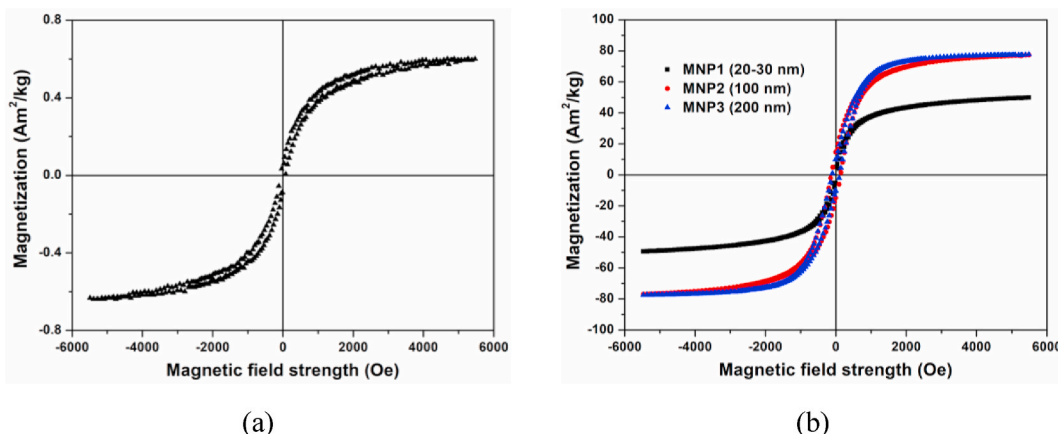

(a)

(b)

Fig. 2. Magnetization versus magnetic field strength curves of (a) Portland cement and (b) nano-Fe$_3$O$_4$ particles. 1 T = 10,000 Oe.
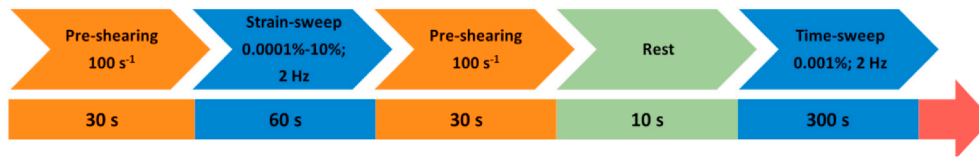
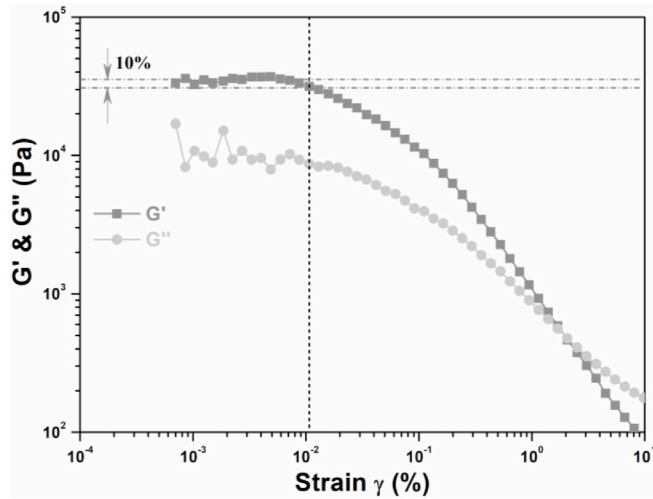**Fig. 4.** Rheological testing protocol used in this study.

Fig. 5. Typical oscillatory strain sweep testing results of cementitious paste (w/c = 0.4, MNP1 = 3%).

$$\tau_{c,ys} = \gamma_c \cdot G' \qquad (4)$$

where $\tau_{c,ys}$ is the elastic limit yield stress (Pa), γ_c is the critical strain (%), and G' is the storage modulus at the critical strain (Pa).

Flow curve test is conducted using fresh samples to measure the dynamic rheological parameters of cement pastes in the absence of magnetic field. After pre-shearing of the sample at shear rate of 100 s^{-1} for 30 s, the shear rate decreases logarithmically from 100 s^{-1} to 0.1 s^{-1}. A typical shear curve of cementitious paste with nano-Fe$_3$O$_4$ particles is shown in Fig. 6. It can be observed that with the decrease of shear rate, the measured shear stress first slowly decreases and then dramatically decreases. At extremely low shear rate (e.g., less than 1 s^{-1}), a slight increase in the shear stress is observed. The plastic viscosity at the linear
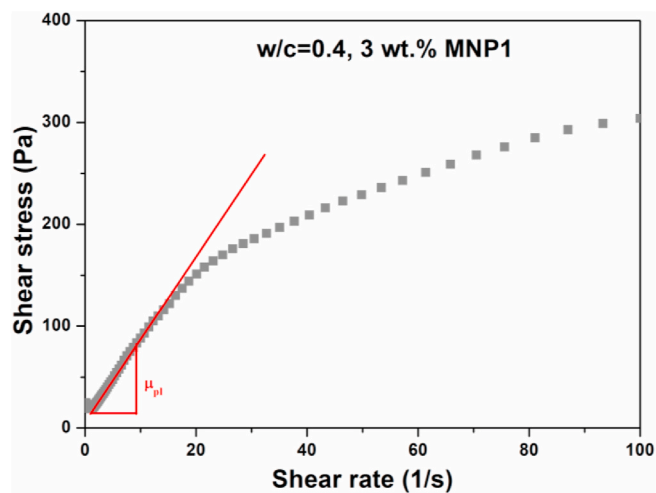

**Fig. 6.** Typical shear curve of cementitious paste with w/c of 0.4 and MNP1 content of 3 wt%.

low shear rate region (i.e. 1-5 s^{-1}) is used as the Bingham plastic viscosity in Eq. (3) to calculate the movement velocity of nanoparticles in cement-based suspensions under external magnetic field [25].

## 3. Experimental results

3.1. Effect of particle concentration

The influences of particle concentration on the structural build-up of cementitious paste are discussed in detail from the perspective of the cementitious pastes containing MNP1. Fig. 7 (a-d) present the early structural build-up illustrated by the evolutions of storage modulus (*G'*) and phase angle (*δ*) for the cementitious pastes with MNP1 concentrations of 0%, 0.25%, 1% and 3%, respectively. For the cement paste without nano-Fe$_3$O$_4$ particles, hereafter named "reference cement paste", the evolution of the storage modulus shows a continuous increase with time and the phase angle gradually decreases and then stabilizes. The continuous growth of the storage modulus indicates the development of structural build-up of cementitious paste over time. The decrease of the phase angle represents the domination duration of colloidal interactions at early age, and the time when the phase angle starts to stabilize is defined as percolation time [23,30], after which cement hydration plays a predominant role in structural build-up. The percolation time characterizes the time for colloidal particles to reach equilibrium. The application of the external magnetic field with 0.5 T shows negligible influences on the general trend of the storage modulus and phase angle. This means that the structural evolution of the reference cement paste is not significantly affected by the external magnetic field, which is in agreement with [16,31]. This can be explained by the magnetic properties of the Portland cement. It can be seen from Table 2 that the saturation magnetization of the Portland cement particles is only 0.59 Am^2/kg, which is significantly lower than that of the nano-Fe$_3$O$_4$ particles (49.48–77.56 Am^2/kg). Accordingly, the reference cement paste shows limited responses to an external magnetic field.
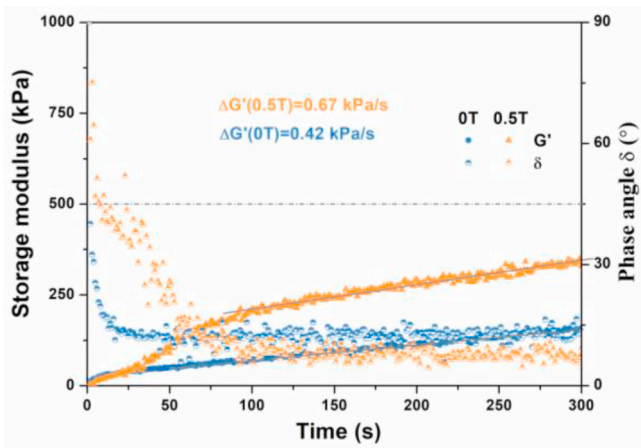
The incorporation of nano-Fe$_3$O$_4$ particles shows significant influences on the thixotropic structural build-up of cementitious paste. To assess the structural build-up rate quantitatively, the increase rate of the storage modulus at steady period (ΔG') is calculated, as presented in Fig. 7. In the absence of an external magnetic field, the magnitude and increase rate of the storage modulus increase with the addition of nano-Fe$_3$O$_4$ particles, especially at higher concentration, indicating higher and faster structural build-up of the cementitious paste. After adding nano-Fe$_3$O$_4$ particles into cement paste medium, the nanoparticles can be regarded as randomly distributed in cementitious suspensions. On the one side, the free water with lubricating effect is declined. On the other side, the average distance between solid particles is reduced and the inter-particle contacts are increased. This increases the colloidal interactions between solid grains, resulting in stronger flocculation structure and stiffness of the cementitious suspension. In addition, the nano-Fe$_3$O$_4$ particles have a tendency to agglomerate due to their high magnetic properties [32,33], which is expected to contribute to the enhancement of the solid-like properties. The increased structural build-up rate at steady state after adding nano-Fe$_3$O$_4$ particles is probably contributed by the nucleation effect of the nanoparticles, providing more nuclei for C-S-H hydrates. Despite the high stiffness of the cementitious pastes with nanoparticles, it seems that higher nanoparticles addition results in slightly shorter percolation time. This
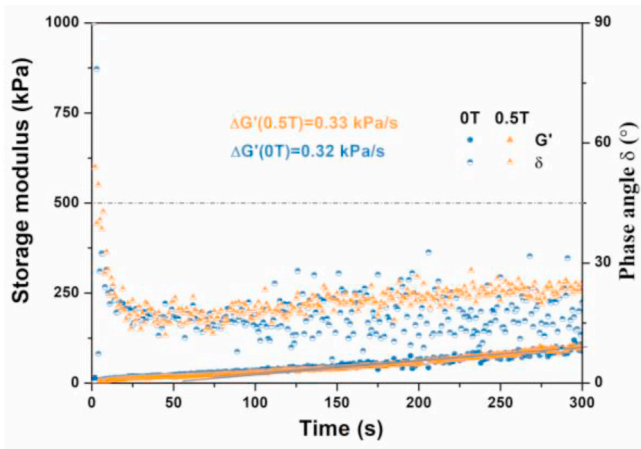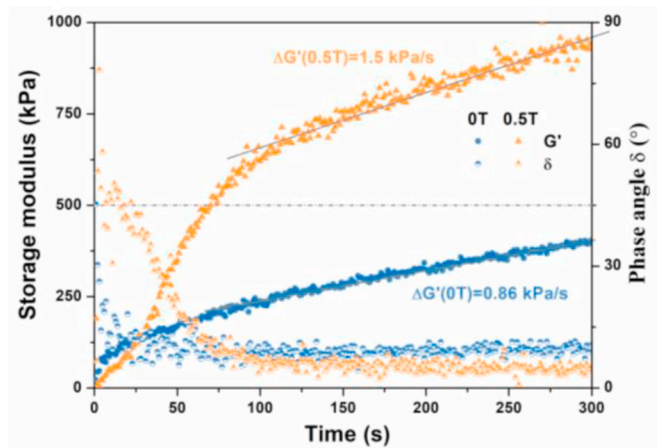
(a) 0% MNP1
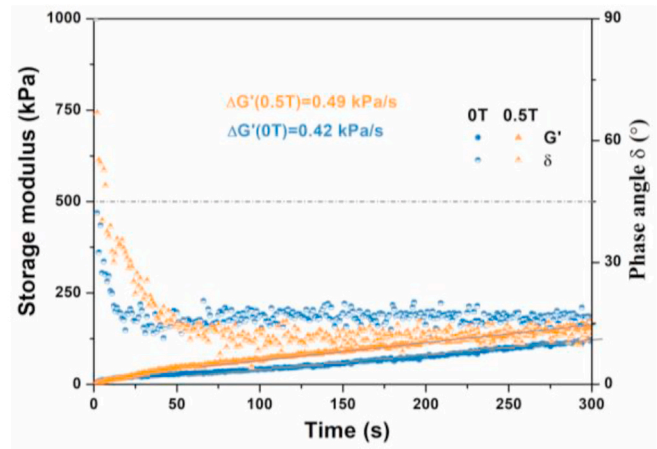
(b) 0.25% MNP1

(c) 1% MNP1

(d) 3% MNP1

Fig. 7. Influence of particle concentration on early structural evolution of cementitious paste. ΔG′ is the increase rate of the storage modulus at steady state.

implies that the cementitious pastes with nano-Fe_3O_4 particles have faster formation rate of flocculation structures comparing with the reference cement paste due to the improved colloidal interactions.

After applying a magnetic field with 0.5 T, all the cementitious pastes containing nano-Fe_3O_4 particles exhibit obvious rheological responses. This can be described by the following general aspects. At magnetization time around a few seconds, the phase angle is above 45°, and the storage modulus of the cementitious pastes under magnetic field is lower than that obtained without magnetic field. The loss modulus, as shown in Fig. 8, gradually increases with the magnetization time. This indicates that the cementitious pastes containing nano-Fe_3O_4 particles exhibit an immediate liquid-like behavior domination right after initiation of the external magnetic field. On the other hand, after experiencing enough period of magnetization, the storage modulus significantly increases, and the phase angle gradually decreases to be stabilized. At steady state, the magnitude of the phase angle in the presence of the external magnetic field is lower than that without magnetic field, whereas the increase rate of the storage modulus shows an opposite behavior. From the viewpoint of loss modulus, it reaches a peak and then reduces to a stable value. All the indicators mean that the application of the external magnetic field for a longer period increases the stiffness of the cementitious paste. In a word, in the presence of an external magnetic field, the liquid-like properties dominate the solid-like properties at the very early stage, while the solid-like behavior becomes more dominant with magnetization time. This behavior can be respectively attributed to the
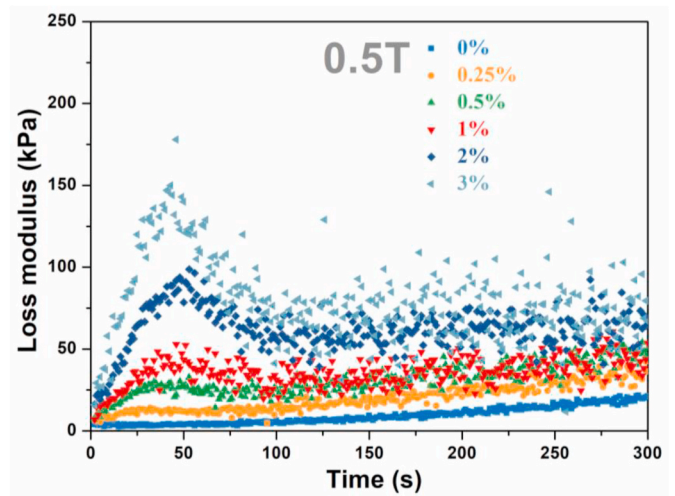

Fig. 8. Influence of particle concentration on the evolution of loss modulus under external magnetic field of 0.5 T.

movement of the nano-Fe$_3$O$_4$ particles and the formation of magnetic clusters under external magnetic field [21,25].

The intensity of the magneto-rheological response magnifies with the concentration of the nano-Fe$_3$O$_4$ particles. More specifically, the differences of the storage modulus under magnetic field of 0 T and 0.5 T are enlarged with increasing concentration of the nanoparticles, regardless of the magnetization time. In the presence of the external magnetic field, with the increase of nano-Fe$_3$O$_4$ particles content, the phase angle at steady state gradually decreases and the increase rate of the storage modulus increases. Moreover, higher nano-Fe$_3$O$_4$ concentration results in longer time for the phase angle to reach 45°, higher increase rate of the loss modulus at early age as well as larger peak value of the loss modulus, as presented in Fig. 8. These results indicate that increasing nano-Fe$_3$O$_4$ concentration increases the intensity of liquid-like properties immediately after introduction of the magnetic field and enhances the stiffness of the cementitious paste after undergoing longer magnetization. It should be mentioned that the time for the loss modulus to reach the peak does not seem to show a linear correlation with the concentration of the nano-Fe$_3$O$_4$ particles. Instead, under the magnetic field of 0.5 T, increasing nano-Fe$_3$O$_4$ concentration from 0.25% to 1% leads to a slight increase in peak time, while it shows negligible change when the nano-Fe$_3$O$_4$ particles content further increases to 3%.

The possible explanations for the higher magneto-rheological response at higher nano-Fe$_3$O$_4$ particles content can be illustrated by the solid particle movement and chains or clusters formation under external magnetic field. Upon magnetization, the nano-Fe$_3$O$_4$ particles have a potential to move to assemble chains or clusters under the external magnetic field. This creates a sort of mechanical micro-agitation effect, probably breaking the weak connections between cement particles, which are widely recognized as C-S-H bridges [27,34], and possibly releasing entrained water in agglomerated structures. With the increase of concentration, more nano-Fe$_3$O$_4$ particles will try to move to join the clusters, possibly resulting in stronger micro-agitation effect. As a result, the probability of destruction of C-S-H bridges increases with the concentration of nano-Fe$_3$O$_4$ particles, and thus higher liquid-like behavior can be observed. After longer period of magnetization, the cementitious paste containing nano-Fe$_3$O$_4$ particles exhibits higher stiffness due to the presence of magnetic chains or clusters. The interparticle force induced by magnetic field increases with the decrease of distance between magnetic particles [35]. With increasing nano-Fe$_3$O$_4$ concentration, on the one side, the number of nanoparticles contributing to the magnetic clusters increases, leading to larger sizes of magnetic clusters. On the other side, the interaction between magnetic nanoparticles is enhanced, due to the reduction in the distance between nano-Fe$_3$O$_4$ particles and their mutual inductive effect. Accordingly, stronger solid-like properties are obtained at higher nanoparticles concentration. Furthermore, the magneto-rheological responses of cementitious paste increase with increasing magnetic field strength from 0 T to
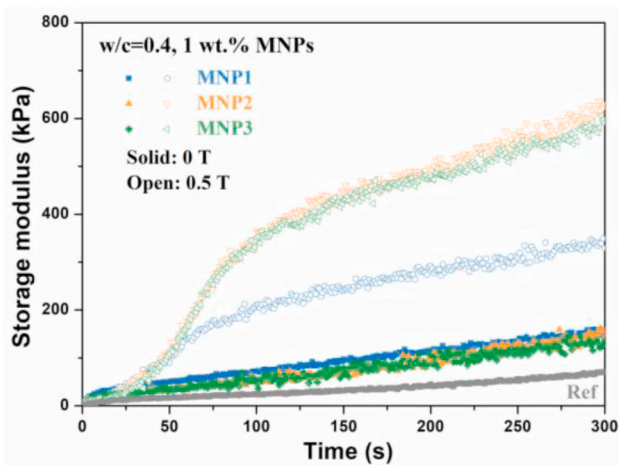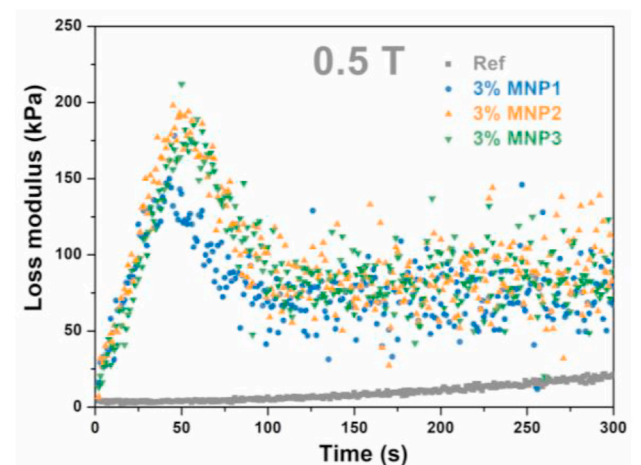

(a) Storage modulus (1 wt.%)
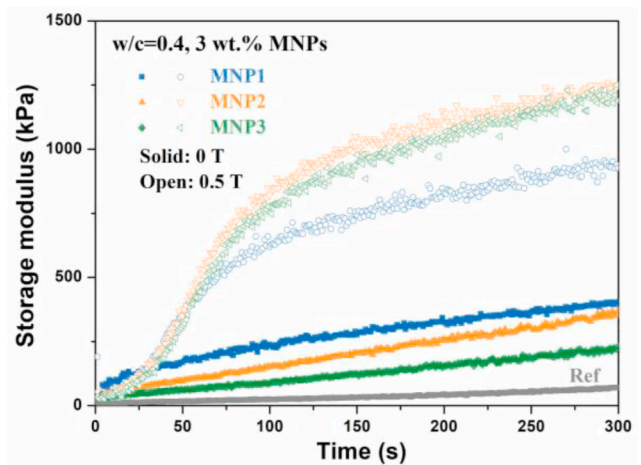
(b) Storage modulus (3 wt.%)
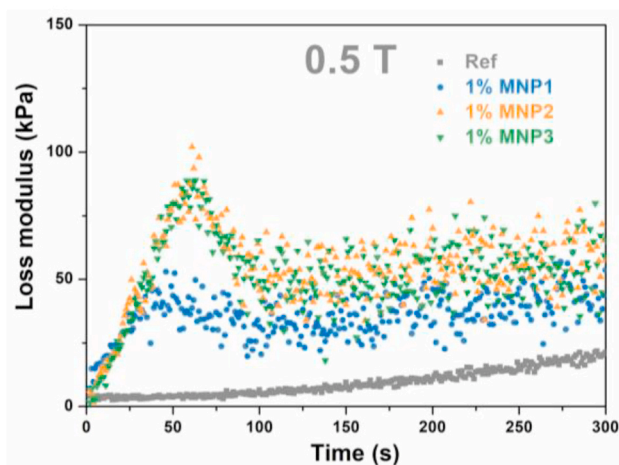
(c) Loss modulus under 0.5 T (1 wt.%)

(d) Loss modulus under 0.5 T (3 wt.%)

Fig. 9. Effect of particle size on the evolution of (a–b) storage modulus and (c–d) loss modulus.

0.75 T [21]. Under the magnetic field of 0.5 T in this study, higher total nanoparticles concentration means higher concentration of remaining nanoparticles in the interstitial solution. More remaining nanoparticles offer more opportunities for the formation of C-S-H hydrates, which possibly could explain the higher increase rate of the storage modulus at steady state with the concentration of nano-Fe_3O_4 particles.

3.2. Effect of particle size

The influences of particle size of nano-Fe_3O_4 particles on the evolution of storage modulus and loss modulus of cementitious pastes with nanoparticles concentration of 1 wt% and 3 wt% are depicted in Fig. 9. Obviously, the structural evolution of the cementitious pastes shows a strong dependence on the particle size of the nanoparticles, regardless of the presence or absence of the external magnetic field. It can be clearly observed from Fig. 9 (a-b) that the addition of nano-Fe_3O_4 particles strengthens the structural build-up of the cementitious paste in the absence of the magnetic field, irrespective of the particle size. The extent of variation of the storage modulus relies on the concentration of nano-Fe_3O_4 particles. In the case of nano-Fe_3O_4 of 1 wt%, the particle size of the nano-Fe_3O_4 particles seems to have little influence on the evolution of the storage modulus. However, at the nano-Fe_3O_4 content of 3 wt%, the cementitious paste containing larger nanoparticles shows lower magnitude of storage modulus. This can be explained by the water film thickness theory [36,37]. The water in well-dispersed cement paste can be divided into two parts, one is for filling the voids between cement particles and another is for coating particles. After adding nanoparticles with ultra-high specific surface area, more water is required to coat the nanoparticles, leading to a relatively low water film thickness of solid particles. Moreover, the number of particles increases with the decrease of particle size under the same weight. This means that smaller nano-Fe_3O_4 particles could create more contacts and frictional interactions between solid particles, exhibiting an increase effect on the structural build-up. Therefore, at the same addition content, higher stiffness can be obtained for the cementitious paste containing nanoparticles with smaller particle size.

In the presence of the external magnetic field, the evolution of the storage modulus at very early age is less dependent on the particle size of the nanoparticles. However, after exposing to the external magnetic field for a longer period, the storage modulus of the cementitious pastes with MNP2 and MNP3 is far higher than that of the cementitious paste containing MNP1. Distinct trends can also be observed from the evolution of the loss modulus in Fig. 9 (c-d). More specifically, the increase rate of the loss modulus at early age is mainly determined by the concentration of the nanoparticles, instead of the particle size. By contrast, the peak values of the loss modulus and the corresponding peak time of cementitious pastes containing MNP2 and MNP3 are higher than that of cementitious paste with MNP1, regardless of the nano-Fe_3O_4 concentration. The results indicate that the cementitious paste containing MNP2 or MNP3 exhibits higher rheological response to the external magnetic field compared with the cementitious paste with MNP1. Most interestingly, the cementitious paste with MNP2 shows similar evolution and magnitude of storage modulus and loss modulus to the paste with same concentration of MNP3. In other words, increasing the particle size from 100 nm to 200 nm has negligible influences on the stiffness and structural evolution of the cementitious paste in the presence of 0.5 T magnetic field.

The different rheological responses of the cementitious paste to the magnetic field (0.5 T) can be explained by the crystalline structures and magnetic properties of the nanoparticles. As shown in Fig. 3, well-defined diffraction peaks of (220), (311), (400), (422), (511) and (440) planes, corresponding to the spinel cubic structure of standard magnetite (JCPDS File No. 19–0629) [38], can be observed for all the nano-Fe_3O_4 particles. Strong and sharp peaks indicate highly crystalline nature of the magnetite, and thus highly magnetic properties of the nano-Fe_3O_4 particles [39]. The XRD patterns show that MNP2 and

MNP3 have similar crystalline properties, which are significantly higher than MNP1. From Fig. 2, we can see that the magnetization of MNP1, MNP2 and MNP3 at the magnetic field of 0.5 T is 49.43 Am^2/kg, 76.84 Am^2/kg and 77.22 Am^2/kg, respectively. The results provide a solid evidence for the well agreement between the crystalline structures and the magnetic properties of the nano-Fe_3O_4 particles. In the case of cementitious suspensions, the magnetic force between two neighboring nano-Fe_3O_4 particles has a positive correlation with the magnetization, independent of the particle size [25]. That is, under specific magnetic field, MNP2 has a comparable interparticle force to MNP3, which is much higher than MNP1. In combination with the rheological results, it can be obviously observed that the sequences of the magneto-rheological responses are in good agreement with that of the magnetization at 0.5 T. The results can be concluded that the crystalline structures and magnetic properties of the nano-Fe_3O_4 particles play more dominant roles in the structural build-up than particle size under the same external magnetic field. As stated earlier, the increase rate of the loss modulus at early age is nearly independent of the particle size and magnetic properties at the same nano-Fe_3O_4 concentration. The increase of loss modulus represents the cement particles disturbed by nanoparticles micro-agitation reaching their new equilibrium positions, as well as the possible movement of part of nanoparticles [25]. The results to a certain extent indicate that the micro-agitation of moving nanoparticles mainly occurs at the beginning of applying the magnetic field, which is consistent with MR fluids [12,40]. Nevertheless, the increase rate of loss modulus at very early stage can be used as a responsive parameter to characterize the movement velocity of nanoparticles, which will be discussed in the following sections.

Magneto-rheological effect describes the changes of rheological properties of MR fluids before and after applying external magnetic field. In this study, the difference of the storage modulus at magnetization time of 300 s between 0.5 T and 0 T, defined as *D-value*, is selected as a quantitative parameter to describe the magneto-rheological effect of cementitious paste containing nano-Fe_3O_4 particles. The effect of particle size on the magneto-rheological effect of cementitious paste at various nano-Fe_3O_4 concentrations is shown in Fig. 10. Generally, the magneto-rheological effect is considered to show a positive correlation with the concentration of the nano-Fe_3O_4 particles. The cementitious pastes containing coarser nanoparticles (MNP2 and MNP3) exhibit higher magneto-rheological effect than that of the cementitious pastes with finer nanoparticles (MNP1), due to the relatively high magnetic properties. Another reason is the fact that the cementitious pastes with MNP1 possess relatively high rigidity in the absence of the magnetic field. Particle concentration plays a significant role in the influence of
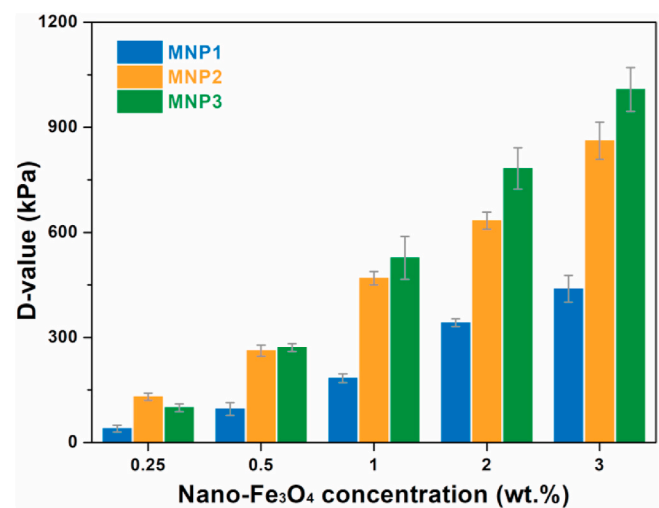

Fig. 10. Effect of particle size on magneto-rheological effect of cementitious paste. Error bar is the standard deviation.

MNP2 and MNP3 on the magneto-rheological effect. At relatively low nanoparticles concentration, the cementitious pastes with MNP2 show approximately similar magneto-rheological effect to the pastes with MNP3. However, at the nanoparticles content higher than 1 wt%, the magneto-rheological effect of the pastes with MNP3 is slightly higher than that of MNP2-containing pastes. This can be attributed to the difference of viscoelastic properties of the cementitious pastes without magnetic field. The storage modulus shows less difference under low nanoparticles addition, whereas larger particles result in smaller storage modulus in the case of relatively high nanoparticles concentration. Accordingly, the concentration-dependent magneto-rheological effect is observed.

Overall, the particle size plays a major role in dominating the viscoelastic properties of cementitious paste without magnetic field, and the response of the cementitious paste to an external magnetic field is mainly determined by the crystalline structures and magnetic properties of the nanoparticles. It can be concluded that cementitious paste containing nano-Fe_3O_4 particles with larger particle size and higher magnetic properties exhibits increased magneto-rheological effect.

4. Theoretical discussion

4.1. Magnetic yield parameter and movement velocity of nanoparticles

In the presence of an external magnetic field of 0.5 T, the magnetic yield parameter and movement velocity of nanoparticles are respectively calculated by Eqs. (1) and (3), and then listed in Table 3. The results first show that the calculated magnetic yield parameters (Y_M^*) for all mixtures are larger than 1, indicating that all the cementitious pastes containing nano-Fe_3O_4 particles can show a response to the external magnetic field. The magnetic yield parameter gradually increases with the increase of nanoparticles concentration for each batch of cementitious pastes, which coincides with the experimental results that the magneto-rheological effect strengthens with the concentration of nano-Fe_3O_4 particles. At the same concentration of nanoparticles, the cementitious paste containing MNP2 has comparable magnitude of magnetic yield parameter to the paste with MNP3, which is far higher than that of the mixture with MNP1. This means that the cementitious pastes containing MNP2 or MNP3 exhibit comparable higher magneto-rheological response than the cementitious paste with same content of MNP1. All the aforementioned statements about the calculated magnetic yield parameter are in good agreement with the experimental results, which provides a theoretical support for the explanation and verification of the magneto-rheological response of cementitious pastes with particle size and concentration.

According to Eq. (3), the movement velocity of the nanoparticles has a linear relationship with the particle size. Consequently, cement-based suspensions with larger nanoparticles generally show relatively higher movement velocity of nanoparticles. Under the external magnetic field of 0.5 T, the movement velocity of nanoparticles gradually increases with the concentration for each batch of cementitious paste, indicating a higher probability for the destruction of C-S-H bridges between cement particles. This is in good agreement with the experimental results of the loss modulus under external magnetic field, which show that higher nanoparticles concentration results in larger increase rate of loss modulus at early age, i.e. higher liquid-like behavior immediately after initiation of the external magnetic field. Furthermore, the movement velocity of nanoparticles has comparable magnitude to the surface distance between adjoining nanoparticles in Table 3, especially at higher concentrations. This indicates that the facilitation of nano-Fe_3O_4 particles to assemble magnetic clusters by applying magnetic field occurs very fast. This grants an evidence for the concentration-dependent (instead of size- or magnetic property-dependent) evolution of the loss modulus of cementitious paste.

It should be noted that higher movement velocity of the nanoparticles does not necessarily mean higher structural build-up of the cementitious paste. Take the suspensions with nanoparticles concentration of 3 wt% as example, the movement velocity of MNP1, MNP2 and MNP3 in the cement-based suspensions is 43.79 nm/s, 355.51 nm/s and 817.79 nm/s, respectively. However, the storage modulus of the corresponding cementitious pastes at magnetization time of 300 s is ~940 kPa, ~1250 kPa, and ~1230 kPa, respectively. The results to a certain extent reveal that the evolution of storage modulus of the cementitious paste under an external magnetic field is mainly controlled by the crystalline structures and magnetic properties of the nano-Fe_3O_4 particles, rather than their particle size.

4.2. Relationship between calculated theoretical parameters and rheological parameters

Theoretically, higher magnetic yield parameter means greater predomination of magnetic force over the resistance induced by the viscoelastic stress of the suspension, and thus more obvious magneto-rheological response. From the experimental and calculation results, it can be concluded that both the magnetic yield parameter and the magneto-rheological effect show an amplification trend with the increase of nanoparticles concentration for the cementitious pastes containing the same type of nano-Fe_3O_4 particles. The points of D-value

Table 3
Calculated magnetic yield parameters and movement velocities of nanoparticles.

MNPs	Concentration/(%)	M (0.5T)/(Am²/kg)	h/(nm)	$\tau_{c,ys}$/(Pa)	μ_{pl}/(Pa.s)	Y_M^*	$v/(10^{-9}\,m/s)$
MNP1	0.25	49.43	141.75	1.07	6.18	1.48	0.69
	0.5	49.43	107.43	1.61	5.68	2.47	3.48
	1	49.43	80.23	1.96	5.98	5.09	11.18
	2	49.43	58.72	3.65	6.51	6.83	27.24
	3	49.43	48.31	4.52	7.21	9.38	43.79
MNP2	0.25	76.84	566.99	0.98	5.44	3.90	17.44
	0.5	76.84	429.70	1.22	5.19	7.88	53.96
	1	76.84	320.92	1.42	7.25	17.01	104.43
	2	76.84	234.86	1.33	8.31	45.34	236.32
	3	76.84	193.21	1.92	9.43	53.48	355.51
MNP3	0.25	77.22	1134.00	1.03	5.66	3.76	33.43
	0.5	77.22	859.41	1.07	5.53	9.09	104.25
	1	77.22	641.84	1.04	6.11	23.50	254.60
	2	77.22	469.73	1.39	6.38	43.81	621.24
	3	77.22	386.42	1.81	8.29	57.10	817.79

Note: M is the magnetization per unit mass of the nanoparticles at 0.5 T (Am²/kg). h is the distance between nanoparticles (m), which are considered to be arranged in the voids between cement particles as simple cubic order with same inter-particle distance [24,25]. $\tau_{c,ys}$ is the elastic limit yield stress (Pa). μ_{pl} is the plastic viscosity (Pa.s) at linear low shear rate region (i.e. 1-5 s⁻¹). The particle size d in estimating the movement velocity is 25 nm, 100 nm and 200 nm for the nanoparticles of MNP1, MNP2 and MNP3, respectively.

versus magnetic yield parameter are depicted in Fig. 11. It can be seen that the *D-value* shows a good linear relationship with the magnetic yield parameter for each batch of cementitious pastes, with the coefficient of determination R^2 higher than 0.9. Cementitious pastes containing nano-Fe_3O_4 particles with larger size and higher magnetic properties generally have higher magnetic yield parameters and *D-values*. The linear correlation indicates that the calculated magnetic yield parameter can be used to predict the magneto-rheological effect of cementitious pastes with various contents of specific magnetic nanoparticles. In other words, the influence of particle concentration and viscoelastic properties (which is concentration-dependent) of pastes containing specific nano-Fe_3O_4 particles on the magneto-rheological properties can be converted into one influencing factor, i.e. magnetic yield parameter.

The increase of loss modulus of the cementitious paste after applying a magnetic field, describing the improvement of liquid-like properties, is a result of nanoparticles rearrangement. The relationship between the increase rate of the loss modulus at early age (e.g., 2–20 s) and movement velocity of nanoparticles is plotted in Fig. 12. It can be observed that the early increase rate of the loss modulus has an apparent linear correlation with the movement velocity for specific nano-Fe_3O_4 particles. According to Eq. (3), the movement velocity of nanoparticles in cement-based suspensions is determined by the concentration, size and magnetic properties of the nanoparticles, as well as the rheological properties of the suspension. For specific nano-Fe_3O_4 particles, higher concentration means higher movement velocity of nanoparticles and more destroyed C-S-H bridges and flocculation structures between cement particles. Accordingly, higher increase rate of the loss modulus and more liquid-like behavior can be achieved. At the same particle concentration, larger particle size results in a significantly higher movement velocity, and the early increase rates of the loss modulus, however, are almost in the same order of magnitude, which can be clearly observed from Fig. 9 (c-d). As concluded before, the formation of magnetic clusters after applying an external magnetic field is quite fast. The variation of the monitored loss modulus is a post-effect of the displacement of nanoparticles. Therefore, the increase rate of the loss modulus at early age seems to be mainly controlled by the particle concentration, rather than the particle size or magnetic properties. This can be observed from the inserted relationship between the early increase rate of the loss modulus and the particle concentration in Fig. 12. Nevertheless, the movement velocity of nanoparticles is an effective parameter to characterize the improvement of liquid-like behavior of cementitious pastes with specific nano-Fe_3O_4 particles.

5. Conclusions

In the present study, the effects of concentration and particle size of nano-Fe_3O_4 particles on the evolution of structural build-up of cementitious pastes under magnetic field were experimentally investigated, and then correlated to the calculated magnetic yield parameter and movement velocity of nanoparticles. Based on the results and discussion, the following conclusions can be reached:

(1) The application of an external magnetic field with 0.5 T shows negligible influences on the structural evolution of reference cement paste due to the low magnetic properties of the Portland cement particles.

(2) In the absence of a magnetic field, both the stiffness and the formation rate of flocculation structure of cementitious paste increase with the concentration of nano-Fe_3O_4 particles. Under an external magnetic field of 0.5 T, increasing nanoparticles concentration increases the intensity of liquid-like properties immediately after initiation of the magnetic field and enhances the stiffness of cementitious paste after undergoing longer magnetization, due to a large number of available nanoparticles contributing to the formation of magnetic clusters.
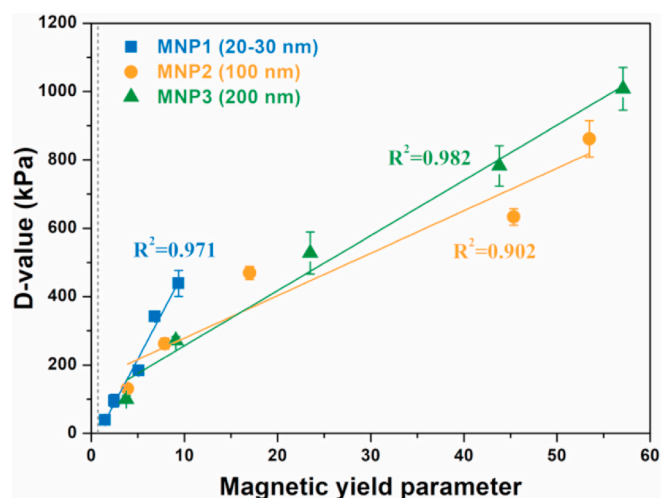

Fig. 11. Relationship between *D-value* and magnetic yield parameter. Error bar is the standard deviation.
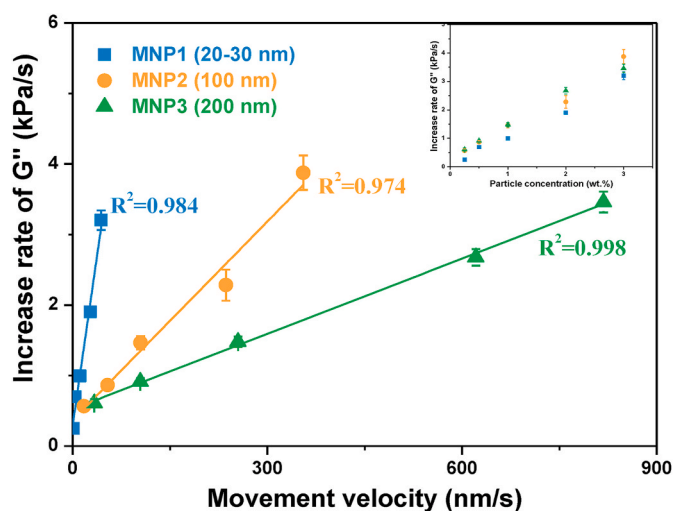

Fig. 12. Relationship between increase rate of loss modulus at early age and movement velocity of nanoparticles. Error bar is the standard deviation.

(3) The particle size plays a considerable role in dominating the viscoelastic properties of cementitious paste without magnetic field. The response of cementitious paste to external magnetic field is mainly determined by the crystalline structures and magnetic properties of the nano-Fe_3O_4 particles. Cementitious pastes containing nano-Fe_3O_4 particles with larger particle size and higher magnetic properties generally exhibit more obvious magneto-rheological effect.

(4) The magnetic yield parameter can be used to predict the magneto-rheological effect of cementitious pastes with various concentrations of specific magnetic nanoparticles. The increase rate of the loss modulus at early age shows an apparent linear correlation with the movement velocity of specific nano-Fe_3O_4 particles.

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

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