

Effect of Solid Volume Fraction on the Magnetorheological Response of Nano-Fe₃O₄ Incorporated Cementitious Paste

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Abstract: Magneto-induced rheology control is beneficial to overcome the opposing property requirements in different construction processes. The viscoelastic properties of paste medium have great effects on the movement and distribution of magnetic particles when applying an external magnetic field and thus the degree of the rheological response. In the present research, the effect of (total) solid volume fraction ϕ_T on the magnetorheological (MR) response of nano-Fe₃O₄ incorporated cementitious paste, represented by the early structural build-up is experimentally investigated. Cementitious pastes with various solid volume fractions are achieved by changing the water-to-cement ratio (w/c) of the paste medium while the nano-Fe₃O₄ concentration remains unchanged. Results reveal that cementitious pastes with extremely low solid volume fractions acting as a dilute suspension show an insignificant increase in stiffness after applying an external magnetic field of 0.5 T, possibly due to the high surface to the surface separation distance between cement particles. Both the magnetic force between neighboring nanoparticles and the viscoelasticity of the suspension increase with increased solid volume fraction. At moderate solid volume fractions (e.g., $0.3 < \phi_T < 0.45$), the formed magnetic clusters fill the voids between cement particles and thus increase the stiffness of the cementitious paste significantly. At relatively high solid volume fractions, despite the high magnetic force between nanoparticles, the dense particle packing limits the formation of magnetic clusters, and the MR response becomes indistinct. For the used cement and nano-Fe₃O₄ particles, the suitable w/c of cementitious paste with pronounced MR response is in the range of 0.4–0.5. DOI: 10.1061/(ASCE)MT.1943-5533.0004440. This work is made available under the terms of the Creative Commons Attribution 4.0 International license, <https://creativecommons.org/licenses/by/4.0/>.

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Introduction

Active rheology control is a ground-breaking concept aiming at triggering the rheological properties and stiffness of fresh

cement-based materials to meet the contradicting property requirements in different processes such as pumping and formwork casting (De Schutter and Lesage 2018; De Schutter et al. 2018; Jiao et al. 2021a). The active rheology control can be achieved by applying an external trigger signal (e.g., magnetic field) to cementitious materials containing responsive chemical polymers or mineral additives (Lesage and De Schutter 2020; Nair and Ferron 2014). The signal can be applied postmixing, i.e., during pumping and formwork casting processes. This means that the active rheology control can be used to adjust the properties on-demand for the same concrete mixture. The active rheology control has a great capacity to become the mainstream of future casting techniques of cement-based materials, making pumping, casting, and 3D concrete printing more reliable and smarter (Reiter et al. 2020; Sanjayan et al. 2021; De Schutter et al. 2019).

One potential approach to achieving active rheology control is adding magnetic particles or additives in combination with exploiting an external magnetic field (Jiao 2021). Fresh cement paste containing magnetic particles acts as a magnetorheological (MR) fluid (Nair and Ferron 2016), in which the rheological properties can be artificially and reversibly controlled by activating a magnetic field. Note that the rheological response of plain cement paste is not significantly affected by the presence of a magnetic field (Nair and Ferron 2014; Jiao et al. 2021f). From the structural build-up perspective, the evolution of the storage modulus of cementitious paste with magnetic nano-Fe₃O₄ particles decreases immediately after applying an external magnetic field (Jiao et al. 2019, 2021c). After a longer period of magnetization, a significant increase in the storage modulus is observed due to the formation of magnetic clusters (Jiao et al. 2021b). The degree of the MR behavior of cementitious

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paste with nano-Fe₃O₄ particles depends on the magnetic field and intrinsic nature of the nanoparticles. Specifically, weak magnetic fields have negligible influences on the rheological responses, while under sufficiently high magnetic fields, the MR response of cement paste increases with the increase of magnetic field strength (Jiao et al. 2020, 2021e). Compared to the particle size, the MR responses of cementitious paste are mainly governed by the magnetic properties and crystalline structures of nano-Fe₃O₄ particles (Jiao et al. 2021d).

The viscoelastic properties and stiffness of cement paste medium have great influences on the movement and distribution of magnetic nanoparticles when applying an external magnetic field and thus the magnetorheological response. At the same nano-Fe₃O₄ particles concentration and without a superplasticizer, cementitious paste with a water-to-cement (w/c) ratio of 0.4 shows a higher MR response than that of cementitious paste with w/c of 0.35, which is attributed to the reduced viscoelastic properties of the system in the absence of magnetic field (Jiao et al. 2021c). However, further findings on the influence of paste medium on the MR response are not available. It is well recognized that cement paste transforms from dilute to concentrated suspension with the increase of solid volume fraction, exhibiting an exponential increase in viscosity and yield stress (Krieger and Dougherty 1959; Mahaut et al. 2008a; Roussel et al. 2010). In the context of the unclear understanding of the MR behavior of cement paste at different particle packing states, it is required to establish the relationship between the MR response and the solid volume fractions of cementitious paste.

This present research examines the influence of solid volume fraction on the structural build-up of cementitious paste with nano-Fe₃O₄ particles under an external magnetic field. The development of storage modulus, loss modulus, and phase angle obtained from the oscillatory time-sweep test is used to describe the early structural evolution of cementitious paste. Cementitious pastes with various total solid volume fractions are achieved by changing the w/c of the medium while maintaining the nano-Fe₃O₄ concentration at 3 wt.%. The magnetic force between neighboring nanoparticles in each cementitious suspension is estimated. The magnetic yield parameter characterizing the relative magnitude of the estimated magnetic force and the resistance induced by the viscoelastic properties of the suspension is calculated. The relationships between MR response, paste stiffness without magnetic field, and magnetic yield parameter are afterward established and discussed. This study allows for a better understanding of the MR response of cementitious paste concerning solid particle packing.

Experimental Program

Materials and Mixture Proportions

Ordinary Portland cement (OPC) CEM I 52.5 N with a specific gravity of 3.20 and an average particle size (D50) of 7.199 μm was used. Table 1 shows the chemical composition, and Fig. 1 presents the particle size distribution of the cement, respectively. nano-Fe₃O₄ particles (MNPs, from US Research Nanomaterials) were used as magneto-responsive additives. The average particle size and specific gravity of the nanoparticles supplied by the manufacturer are 20–30 nm and 4.95, respectively. The saturation magnetization of the Portland cement and nano-Fe₃O₄ particles measured by a vibrating sample magnetometer (VSM-550, Dexion Magnet) is 0.51 and 49.48 emu/g, respectively. All cementitious

pastes were prepared using de-ionized water, and no chemical admixtures were introduced.

Cementitious pastes with various solid volume fractions were determined by changing the w/c of the cement paste medium while the nano-Fe₃O₄ concentration of 3% by mass of the cement paste (i.e., cement + water) remained unchanged. The mixture proportions of the prepared cementitious pastes are shown in Table 2. All cementitious pastes were mixed using a rotational rheometer (MCR 52, Anton Paar) equipped with a helix geometry. The details of the geometric parameters of the helix rotator are given in Jiao et al. (2019). After adjusting the helix rotator to the measurement position, the shear rate increased linearly up to 3,000 rpm within 30 s and then continuously mixed at this rotational speed for

Table 1. Chemical composition of the used cement

Composition	wt%
SiO ₂	19.4
Al ₂ O ₃	6.04
Fe ₂ O ₃	4.12
CaO	61.5
MgO	1.25
SO ₃	5.35
K ₂ O	0.48
Others	1.86

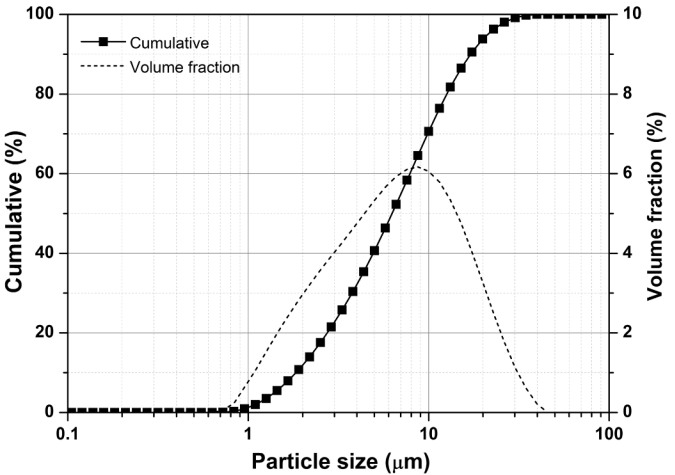


Fig. 1. Particle size distribution of the portland cement.

Table 2. Mixture proportions of cement pastes at various solid volume fractions

No.	ϕ_T^a	OPC (g)	Water (g)	w/c ^b	MNPs (g) ^c
1	0.101	5.00	15.00	3.000	0.6
2	0.211	9.00	11.00	1.222	0.6
3	0.304	12.00	8.00	0.739	0.6
4	0.374	13.00	7.00	0.538	0.6
5	0.417	13.80	6.20	0.449	0.6
6	0.443	14.25	5.75	0.404	0.6
7	0.467	14.65	5.35	0.389	0.6
8	0.490	15.00	5.00	0.333	0.6

^a ϕ_T is the total solid volume fraction, calculated by $\phi_T = (V_{OPC} + V_{MNPs}) / (V_{OPC} + V_{MNPs} + V_W)$ where V_{OPC} , V_{MNPs} , and V_W are the volume of the cement, nano-Fe₃O₄ particles, and water, respectively.

^bw/c is the water-to-cement mass ratio of cement paste medium.

^cThe MNPs content is fixed at 3% by the mass of cement and water.

Table 3. Rheological protocol for evaluating the structural evolution of cementitious paste

No.	Interval	Duration	Parameters	Magnetic field
1	Preshearing	30 s	100 s^{-1}	—
2	Strain-sweep	60 s	0.0001%–10%; 2 Hz	—
3	Preshearing	30 s	100 s^{-1}	—
4	Rest	10 s	—	—
5	Time-sweep	300 s	0.005%; 2 Hz	0 T, 0.5 T

another 120 s. This mixing method provides a repeatable initial state of paste samples for the same mixture proportion (Jiao 2021).

Determination of Structural Build-Up

The structural evolution of cementitious paste under an external magnetic field is evaluated by using a parallel plate rotational rheometer (MCR 102, Anton Paar) equipped with a magnetorheological device (MRD). The diameter of the plate is 20 mm, and the gap between the two parallel plates during the rheological test was fixed at 1 mm. A homogeneous magnetic field of 0.5 T perpendicular to the plate can be generated by setting the current of the electromagnetic coils as 3 A. The rheological protocol measuring the structural evolution of cementitious paste is presented in Table 3. The pre-shearing procedure aims at eliminating the residual stress during gap adjustment and destroying possibly present agglomerated structures. The oscillatory strain-sweep test was used to evaluate the viscoelastic properties of cementitious paste without a magnetic field and determine the linear viscoelastic region (LVER). The shear strain of 0.005% in the oscillatory time-sweep test is within the LVER. No magnetic field was applied during the first four intervals. That is, the sample was started to be imposed in an external magnetic field (0 or 0.5 T) at the beginning of the time-sweep test. Each mixture was measured repeatedly three times using newly-mixed samples. During the entire rheological test, the temperature was maintained at $20^\circ\text{C} \pm 0.5^\circ\text{C}$ by a water bath.

Experimental Results

Viscoelastic Properties of Cementitious Paste without Magnetic Field

Fig. 2 presents the typical oscillatory strain-sweep testing results of the studied cementitious pastes without a magnetic field. It can be seen that the storage modulus of all the cementitious pastes shows linear behavior at relatively low shear strain. As soon as the shear strain reaches a critical value, the storage modulus starts to decline dramatically. This indicates that all cementitious pastes exhibit viscoelastic behavior regardless of the solid volume fractions, which is in agreement with (Schultz and Struble 1993; Conte and Chaouche 2016). As the solid volume fraction increases, the storage modulus at LVER exhibits an increase, indicating an increase in the stiffness. This is due to the improvement of the interparticle contacts and the network strength with increasing solid volume fraction (Roussel et al. 2010; Mahaut et al. 2008b; Jiao et al. 2017).

With regard to the critical strain, it decreases with increasing the solid volume fraction from 0.101 to 0.326. When the solid volume fraction is higher than 0.326, however, the critical strain almost remains unchanged. Similar phenomena were also observed in Yuan et al. (2017), Ukrainczyk et al. (2020), and Mostafa and Yahia (2016), but no detailed explanation was provided. The critical strain from the oscillatory strain-sweep test corresponds to the breakage of early hydration products between cement particles (Roussel et al.

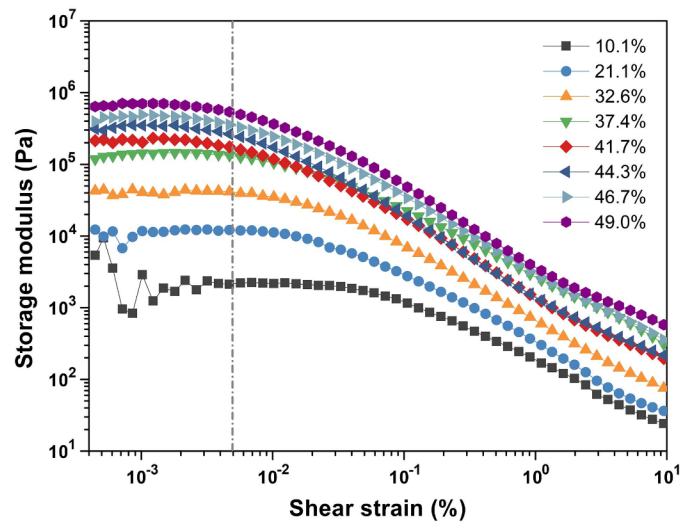


Fig. 2. Typical viscoelastic properties of cementitious paste with various solid volume fractions (MNPs = 3%, without magnetic field).

2012; Huang et al. 2019; Jiao et al. 2021a). Cementitious paste with lower solid volume fraction and higher free water generally has a higher dissolution rate of cement particles and thus a higher concentration of Ca^{2+} ions (Hořková et al. 2009; Liu et al. 2017), resulting in more bridges of initial C–S–H and ettringite. Note that the formation of more hydration products does not necessarily mean a higher stiffness or more solid-like properties of the suspension, as a higher w/c system requires more products to develop a percolating structure due to the larger solid-to-solid spacing (Zhang et al. 2010). Furthermore, the C–S–H gel in a cement paste with a higher particle volume fraction possibly becomes more fragile (Ukrainczyk et al. 2020). Consequently, the deformation capacity of the bridges of early hydration products increases with the decrease of solid volume fraction, and thus a slightly higher critical strain is observed for the cementitious pastes with lower solid volume fraction.

Magnetorheological Response

The rheological response of cementitious paste to an external magnetic field is characterized by the early structural build-up. Fig. 3 shows the evolutions of the structural build-up of cementitious pastes at various solid volume fractions. The cementitious pastes with ϕ_T of 0.101, 0.417, and 0.469 were selected to represent low, moderate, and high solid volume fractions, respectively. It can be seen that the storage modulus, loss modulus, and phase angle of the representative cementitious pastes show distinctly different evolutions with and without an external magnetic field. Specifically, the storage modulus was higher than the loss modulus at the beginning of applying the external magnetic field due to the microagitation effect of the magnetic nano- Fe_3O_4 particles (Jiao et al. 2021c, d). With elapsed time of magnetization, the storage modulus gradually increased, while the loss modulus increases to a peak and then decreases to a steady state. This results in a gradual reduction in the phase angle. After a sufficiently long period of magnetization, e.g., 100 s, the storage modulus under the magnetic field was significantly higher than that without a magnetic field, while the phase angle showed an opposite behavior. This indicates a higher stiffness of the cementitious paste under an external magnetic field, which can be attributed to the formation

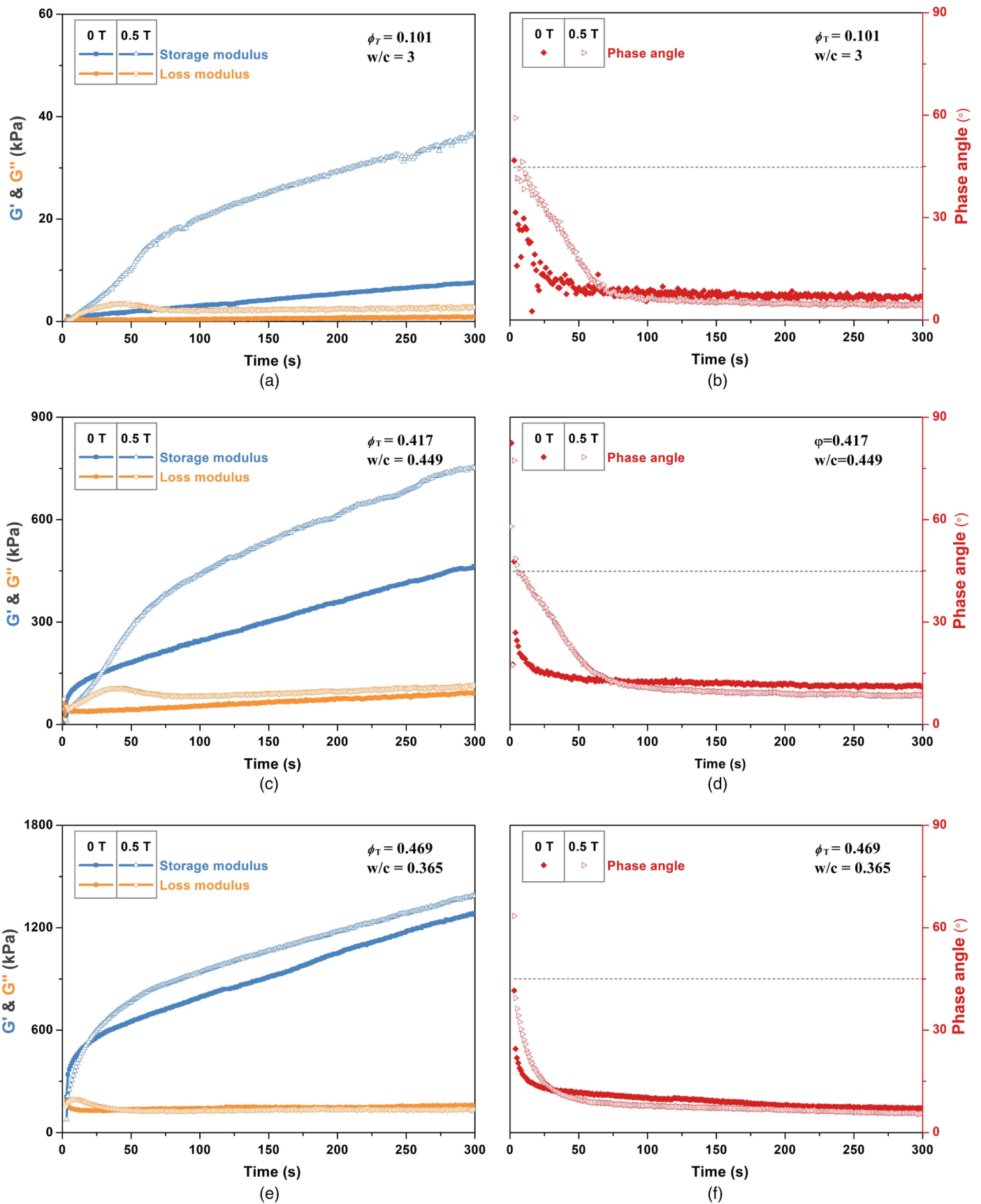


Fig. 3. Early structural evolution of cementitious pastes with various solid volume fractions under external magnetic field: (a) G' and G'' ($\phi_T = 0.101$); (b) phase angle ($\phi_T = 0.101$); (c) G' and G'' ($\phi_T = 0.417$); (d) phase angle ($\phi_T = 0.417$); (e) G' and G'' ($\phi_T = 0.469$); and (f) phase angle ($\phi_T = 0.469$).

of magnetic chains or clusters (Jiao et al. 2019, 2021b; Nair and Ferron 2014).

For the cementitious paste with ϕ_T of 0.101 under an external magnetic field of 0.5 T, despite the significant increase in the storage modulus [e.g., the storage modulus at 300 s (denoted as $G'_{t=300s}$) increasing from 4 to 36 kPa by approx. 800% in Fig. 3(a)], the peak of the loss modulus was less pronounced compared to the cementitious paste with moderate solid volume fraction (i.e., $\phi_T = 0.417$) in Fig. 3(c). Furthermore, it seems that the phase angle of the cementitious paste with ϕ_T of 0.101 required a slightly shorter time to reach a stable state compared to that of paste with ϕ_T of 0.417, as can be observed from Figs. 3(b and d). This indicates that after exposing a cementitious paste to an external magnetic field, the moving nanoparticles and disturbed cement particles (by the microagitation effect) arrive at their equilibrium state more quickly for the cementitious paste with low solid volume fractions possibly due to the relatively low movement resistance. On the other hand, a limited MR response was observed in the cementitious paste with a high solid volume fraction ($\phi_T = 0.469$). More specifically, the increase of the loss modulus only happened at the beginning of applying the external magnetic field, as shown in Fig. 3(e), and it reached its peak very fast compared to the cementitious paste with ϕ_T of 0.417. Meanwhile, the phase angle needs a shorter time to arrive at the steady state in Fig. 3(f). The results indicate that the movement of the nano- Fe_3O_4 particles is possibly limited by the dense packing of the solid particles. Nevertheless, some magnetic clusters of nano- Fe_3O_4 particles still might be formed in the gaps between cement particles, as reflected by the increase in the storage modulus and the slight reduction in the phase angle.

The storage modulus at the end of the time-sweep test (i.e., $G'_{t=300s}$) and the magnetorheological effect of the cementitious pastes are shown in Fig. 4. Two parameters, one is the difference of $G'_{t=300s}$ between 0 and 0.5 T (*absolute MR effect*, kPa) and the other is the relative change of $G'_{t=300s}$ (*relative MR effect*, %), calculated by Eqs. (1) and (2), respectively, are used to describe the MR response of the cementitious pastes

$$\text{Absolute MR effect} = G'_{t=300s}(0.5\text{T}) - G'_{t=300s}(0\text{T}) \quad (1)$$

$$\text{Relative MR effect} = \frac{G'_{t=300s}(0.5\text{T}) - G'_{t=300s}(0\text{T})}{G'_{t=300s}(0\text{T})} \times 100 \quad (2)$$

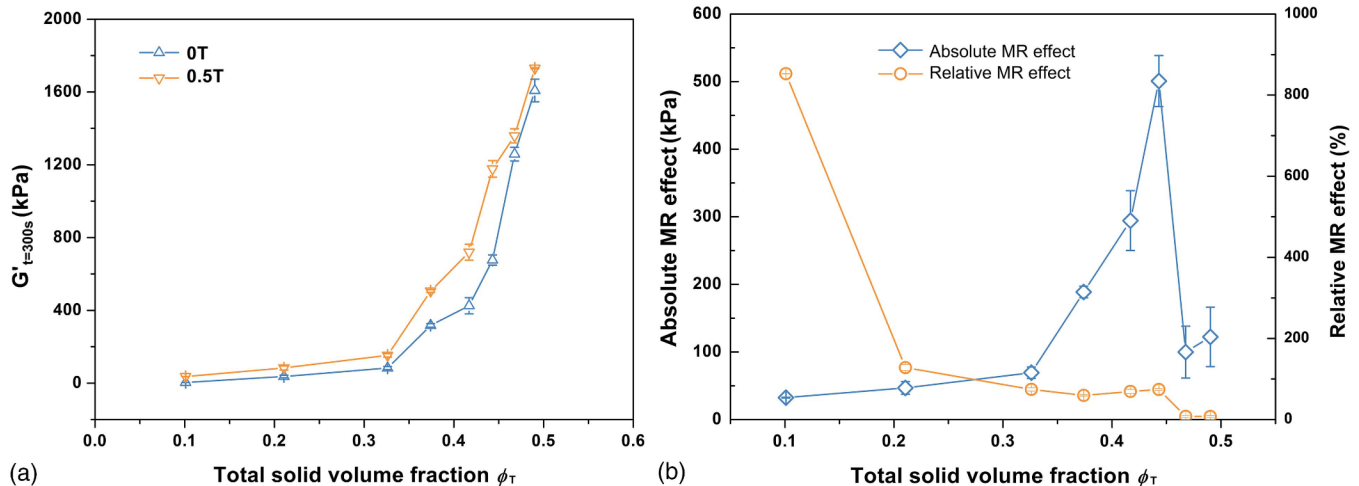


Fig. 4. Effect of total solid volume fraction on: (a) $G'_{t=300s}$; and (b) magnetorheological effect. Error bar is the standard deviation.

where $G'_{t=300s}(0\text{ T})$ and $G'_{t=300s}(0.5\text{T})$ = storage modulus at 300 s under 0 and 0.5 T, respectively. It can be seen that the solid volume fraction can be divided into three regions according to the magnitude of the absolute MR effect. At low solid volume fractions (e.g., $\phi_T < 0.3$), the values of $G'_{t=300s}$ obtained without a magnetic field are in a low magnitude, almost independent of the solid volume fraction. After applying an external magnetic field of 0.5 T, $G'_{t=300s}$ showed a lower increase, and thus only a small difference of $G'_{t=300s}$ was observed. It should be mentioned that the MR response can still be regarded as obvious if described by the relative MR effect [as shown in Fig. 4(b)] because of the extremely low value of the $G'_{t=300s}$ at 0 T. At moderate solid volume fractions (e.g., $0.3 < \phi_T < 0.45$), $G'_{t=300s}$ increases exponentially in the absence of the magnetic field. While under the magnetic field of 0.5 T, the stiffness or solid-like behavior of the cementitious pastes is significantly enhanced. Thereby, the absolute MR effect increases dramatically with increasing solid volume fraction, while the relative MR effect keeps a relatively low value of 0.7 due to high $G'_{t=300s}$ at 0 T. By contrast, at relatively high solid volume fractions (e.g., $\phi_T > 0.45$), the cementitious pastes possess very high stiffness and solid-like properties even without magnetic field, and thus $G'_{t=300s}$ shows less change after applying an external magnetic field of 0.5 T. Consequently, the absolute MR effect decreases and the relative MR effect is almost close to zero, indicating a very limited MR response. In a word, at the same concentration of magnetic nanoparticles, only cementitious pastes with appropriate viscoelasticity can exhibit an obvious rheological response to an external magnetic field.

Discussion

Calculation of Magnetic Force and Magnetic Yield Parameter

The nano- Fe_3O_4 particles are highly magnetic, as can be observed from the high saturation magnetization of 49.48emu/g from the VSM test. After applying an external magnetic field, a magnetic force exists between the nano- Fe_3O_4 particles, and thus the nanoparticles tend to agglomerate into clusters in cementitious suspension. The magnetic force between two neighboring nanoparticles with their centerline following the direction of the magnetic field can be estimated as (Jiao et al. 2021c; Rich et al. 2012)

$$F_{mag} = \frac{\pi d^2 \mu_0 (\rho M)^2}{24} \cdot \left(\frac{6\phi_{MNP_s}}{\pi} \right)^{\frac{4}{3}} \quad (3)$$

where d , ρ , and M = particle size (m), density (kg/m³), and magnetization (Am²/kg) of the nano-Fe₃O₄ particles, respectively; μ_0 = magnetic permeability of vacuum ($4\pi \times 10^{-7}$ N/A²); and ϕ_{MNP_s} = fraction of nanoparticles against the voids between cement particles, calculated by

$$\phi_{MNP_s} = \frac{V_{MNP_s}}{(1 - \phi_C) \cdot V_{Total}} \quad (4)$$

where V_{MNP_s} and V_{Total} = volume of nano-Fe₃O₄ and total paste (kg/m³), respectively; and ϕ_C = volume fraction of cement (%). When the magnetic force overcomes the resistance of the suspension, the nanoparticles can move away from their positions and contact with each other to form magnetic chains and/or clusters. The relative magnitude of the magnetic force and the resistance of the paste can be estimated by the magnetic yield parameter (Jiao et al. 2021c, d)

$$Y_M^* = \frac{\mu_0 (\rho M)^2}{24\tau_{c,ys}} \cdot \left(\frac{6\phi_{MNP_s}}{\pi} \right)^{\frac{4}{3}} \quad (5)$$

where $\tau_{c,ys}$ = shear stress at the critical strain, based on the assumption that the movement resistance exerting to the nanoparticles mainly originates from the bridges of early hydration products between cement particles. If the magnetic yield parameter is higher than 1, the nanoparticles will move to form chains and/or clusters, and the suspension will show an obvious MR response.

In the presence of an external magnetic field of 0.5 T, the estimated magnetic force and calculated magnetic yield parameter of the studied cementitious pastes with various solid volume fractions are shown in Fig. 5. Fig. 5(a) shows that the magnetic force between two adjacent nanoparticles gradually increases with increased total solid volume fraction by affecting the relative volume fraction of the nanoparticles, as can be observed from Eq. (3). The growth rate of the magnetic force speeds up at higher solid volume fractions. This is attributed to the significant reduction of the surface-surface separation distance between nanoparticles. Indeed, as solid volume fraction increases, the volume fraction

of nanoparticles per unit volume of cementitious paste increases and the voids between cement particles decreases, resulting in a significant increase in the relative concentration of nanoparticles to voids between cement particles. The increase of magnetic force indicates that the interparticle connection induced by the external magnetic field is strengthened by increasing the particle packing density of the suspension. Fig. 5(b) shows that the magnetic yield parameter of all the studied cementitious pastes is larger than 1, indicating that all the pastes can exhibit a rheological response to an external magnetic field of 0.5 T. This is in good agreement with the rheological experimental results in Fig. 4. Furthermore, there is a linear relationship between the magnetic yield parameter and the total solid volume fraction, with the coefficient of determination R^2 of 0.96. The complete opposite evolution trend of the magnetic yield parameter than the magnetic force is attributed to the fact that the former term depends not only on the magnetic properties and relative volume fraction of the nano-Fe₃O₄ particles but also on the viscoelastic properties of the suspension.

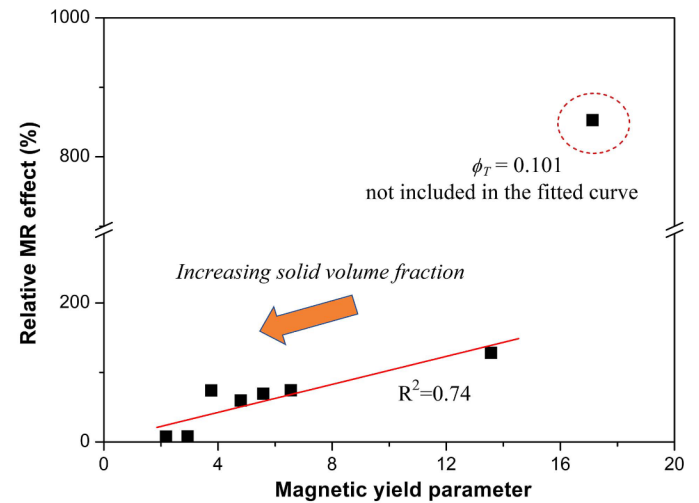


Fig. 6. Magnetic yield parameter versus relative MR effect.

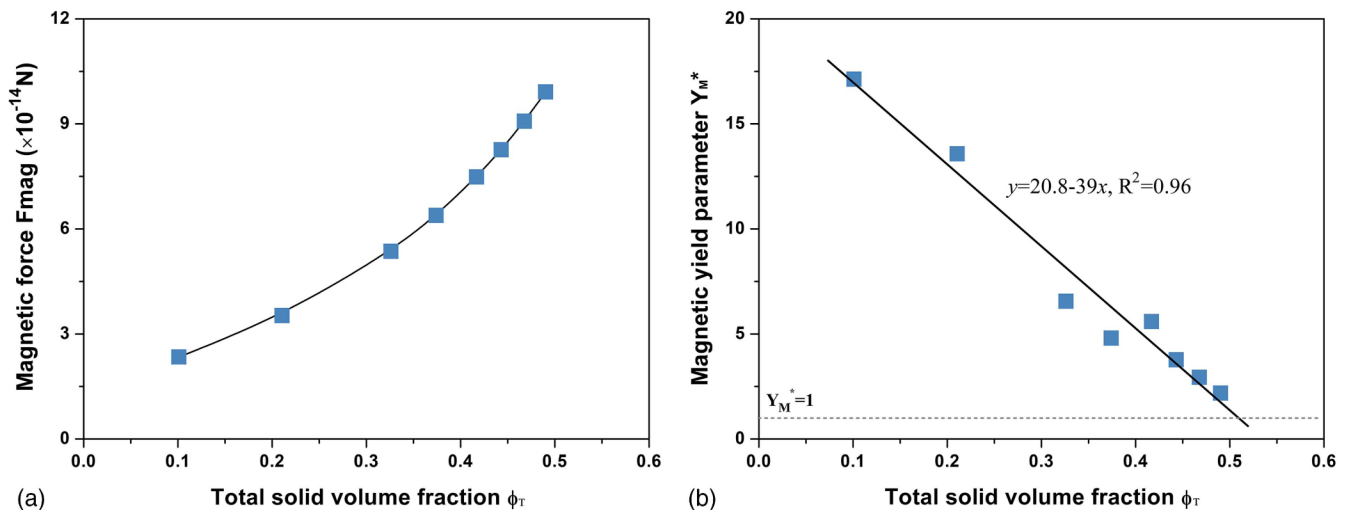


Fig. 5. (a) Magnetic force; and (b) magnetic yield parameter of cementitious pastes at various solid volume fractions, in the presence of a magnetic field of 0.5 T.

Relationship between MR Response, Paste Stiffness without Magnetic Field, and Magnetic Yield Parameter

The MR response of cementitious paste depends on the magnetic force between nanoparticles and the stiffness of the suspension. The relationship between the relative MR effect and the magnetic yield parameter is first established, as presented in Fig. 6. If excluding the cementitious paste with ϕ_T of 0.101, there is a roughly linear relationship between the magnetic yield parameter and the relative MR effect. This indicates that increasing solid volume fraction

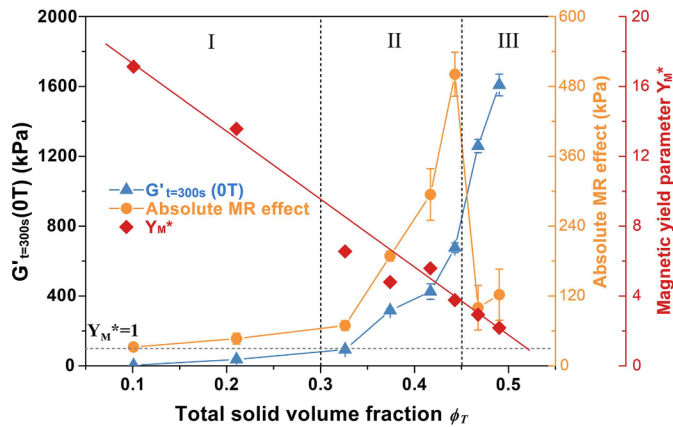


Fig. 7. Correlations between $G'_{t=300\text{ s}}(0\text{ T})$, absolute MR effect, and magnetic yield parameter. Error bar is the standard deviation.

generally decreases the magnetic yield parameter and the MR response, despite the increase in the magnetic force between neighboring nanoparticles. The aberrant point of $\phi_T = 0.101$ is due to the high liquid-like behavior of the suspension without a magnetic field. The results reveal that the estimated magnetic yield parameter to a certain extent provides a theoretical explanation of the MR response of cementitious pastes with various solid volume fractions.

However, the magnetic yield parameter does not fully explain why the absolute MR effect shows a peak response in the vicinity of $\phi_T = 0.443$ [Fig. 4(b)]. It is hypothesized that this behavior is due to the interactions between magnetic clusters and neighboring networks of cement particles. To this end, the relationships between absolute MR effect, paste stiffness without magnetic field, and magnetic yield parameter are subsequently demonstrated, as shown in Fig. 7, where the paste stiffness without magnetic field is characterized by $G'_{t=300\text{ s}}(0\text{ T})$. The schematic diagram illustrating the particle distribution of the system at various solid volume fractions in the absence and presence of a magnetic field is presented in Fig. 8. At relatively low solid volume fractions (e.g., $\phi_T < 0.3$), the cementitious paste without a magnetic field acts as a dilute suspension, as shown in Fig. 8(a), with very high fluidity and liquid-like properties. After applying an external magnetic field of 0.5 T, the magnetic force between adjoining nanoparticles is much larger than the resistance induced by the viscoelastic stress of the suspension, and the nano- Fe_3O_4 particle can contact with each other to form clusters and/or agglomerates in the suspension. However, the formed magnetic clusters probably cannot connect neighboring cement particles due to the large interparticle distance. In this case, the cementitious paste after applying an external magnetic field is

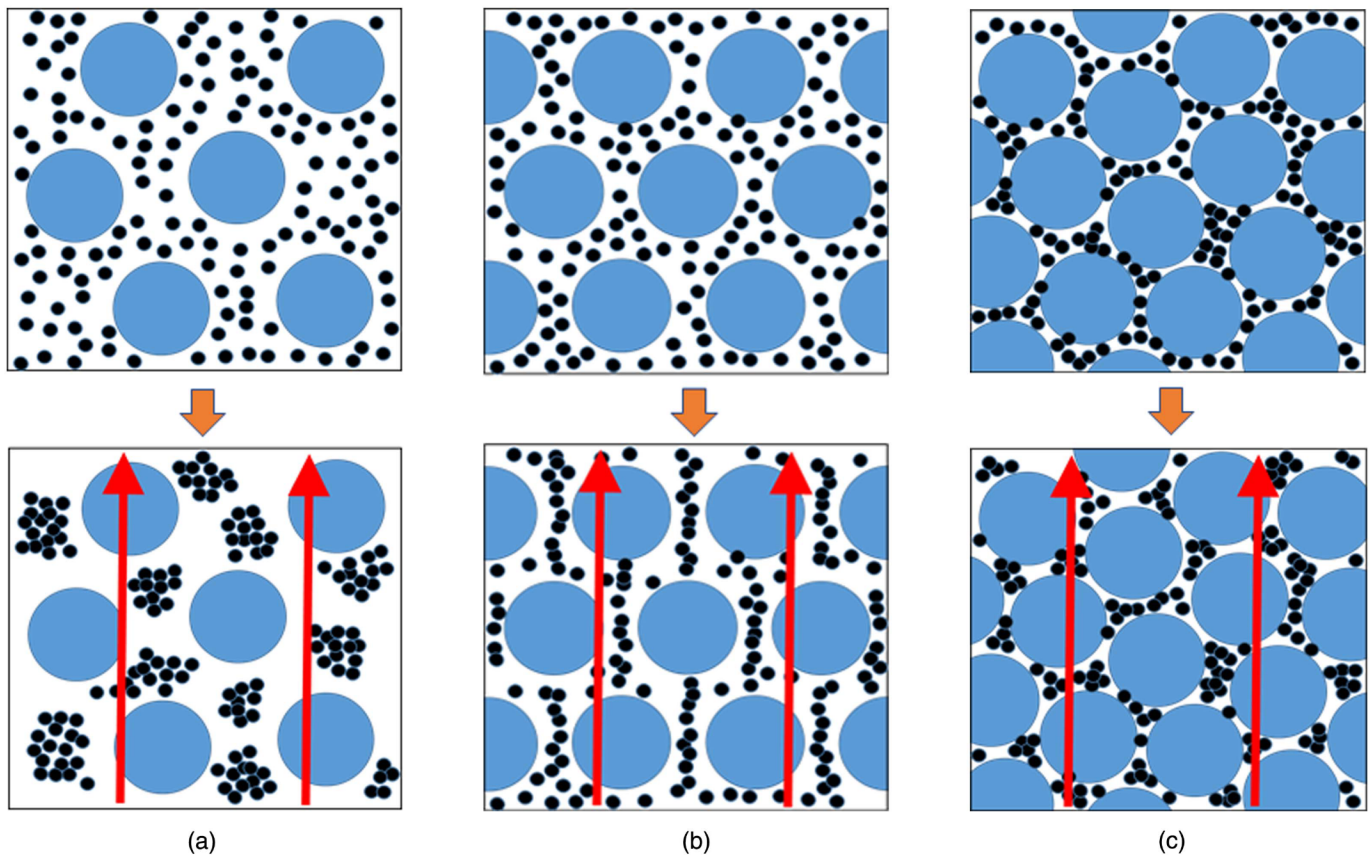


Fig. 8. Schematic diagram of particle distribution at: (a) low ϕ_T ; (b) moderate ϕ_T ; and (c) high ϕ_T . Larger circles indicate cement particles, small dots are nano- Fe_3O_4 particles, and the arrow is the magnetic field.

still regarded as a dilute suspension, and the stiffness cannot increase obviously. Therefore, only a small increase in the difference of $G'_{t=300\text{ s}}$ (i.e., absolute MR effect) is observed at relatively low solid volume fractions.

At moderate solid volume fractions (e.g., $0.3 < \phi_T < 0.45$), the cementitious paste without a magnetic field starts to behave as a concentrated suspension. The interparticle distance gradually decreases, and the stiffness increases with the solid volume fraction. After applying an external magnetic field of 0.5 T, the magnetic force between nanoparticles is higher than the resistance of the suspension. The formed magnetic clusters can fill the voids between cement particles, as presented in Fig. 8(b), connecting the solid particles and thus increasing the stiffness. The absolute MR effect gradually increases with the increase of the total solid volume fraction until an optimal fraction with a maximum difference value of $G'_{t=300\text{ s}}$. At relatively high solid volume fractions (e.g., $\phi_T > 0.45$), the cementitious paste shows very high solid-like behavior without a magnetic field, as reflected by the high storage modulus. After applying an external magnetic field of 0.5 T, the magnetic force between nanoparticles might be higher than the resistance of the paste, and the nanoparticles could move in the suspension. Nevertheless, the high stiffness of the paste hinders the formation of magnetic clusters, as shown in the diagram in Fig. 8(c), and thus the increase of the storage modulus is limited compared to the high storage modulus without a magnetic field. Thereby, the absolute MR effect gradually decreases at relatively high solid volume fractions. It should be mentioned that the cementitious pastes with higher solid volume fractions have relatively higher volume fractions of nanoparticles due to the constant mass concentration of nanoparticles. This further emphasizes the hindering effect of dense solid particle packing. It can be predicted that very dense particle packing can prevent the movement of nanoparticles to form clusters, and in this case, the cementitious paste will not show any rheological response to an external magnetic field. This is to a certain extent evidenced by the experimental results that the MR response weakens with the chemical hydration time (Jiao 2021). Unfortunately, this prediction cannot be perfectly evaluated by the used parallel rheometer due to the high stiffness of the suspension.

Conclusions

The influence of solid volume fraction on the early structural evolution of cementitious paste containing nano- Fe_3O_4 particles is investigated under an external magnetic field. The relationships between magnetorheological (MR) response, paste stiffness without magnetic field, and solid volume fraction are discussed. Based on the experimental results in this study, the following conclusions can be drawn:

1. Without a magnetic field, the stiffness of cementitious paste increases with the solid volume fraction due to the improvement of connections and contacts between solid particles. At low solid volume fractions, the critical strain obtained from the oscillatory strain-sweep test, corresponding to the breakage of links and bridges of early hydration products, is relatively larger compared to that obtained at higher solid volume fractions.
2. For the cementitious paste with low solid volume fractions under an external magnetic field, the moving nanoparticles arrive at their final positions more quickly due to the relatively low movement resistance. However, the stiffness obtained under a magnetic field is still not pronounced, which is possibly attributed to the fact that the formed magnetic clusters cannot connect the neighboring cement particles due to the high surface-surface separation distance.
3. With the increase of solid volume fraction, both the magnetic force between adjoining nano- Fe_3O_4 particles and the viscoelasticity of the suspension increase, while the magnetic force is still higher than the resistance of the suspension. At moderate solid volume fractions (e.g., $0.3 < \phi_T < 0.45$), the formed magnetic clusters fill the voids between cement particles, possibly connecting the solid particles and increasing the stiffness of the suspension, and thus the cementitious paste shows an obvious MR response.
4. At relatively high solid volume fractions, the cementitious paste shows very high solid-like behavior. Despite the higher magnetic force between nanoparticles than the viscoelastic resistance stress, the cementitious suspension limits the formation of magnetic clusters, and the rheological response of the suspension to an external magnetic field becomes indistinct.
5. Under an external magnetic field of 0.5 T, the suitable w/c of cementitious paste with pronounced MR response is in the range of 0.4–0.5 for the used cement and nano- Fe_3O_4 particles. It is inferred that very dense particle packing can prevent the movement of nanoparticles to form clusters, and hence the cementitious paste cannot show any apparent rheological response to an external magnetic field.

Data Availability Statement

All data, models, and code generated or used during the study appear in the published article.

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