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A review of the effect of nanoclays on the fresh and hardened properties of cement-based materials

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ABSTRACT

This paper provides an overview of the use of nanoclays in cement-based materials. The effect of nanoclays on shear rheological properties will be discussed, with a focus on structural build-up behavior. This macroscale flow behavior will then be tied to the effect of nanoclays on the fresh microstructure as characterized via in-situ particle size measurements and rheological techniques. This will provide insight on the mechanisms underlying the effect of nanoclays on fresh state properties through an improved understanding of their effect on flocculation and coagulation behavior. In addition, secondary effects nanoclays have on the hardening and hardened properties will also be discussed. Examples of casting applications in which nanoclays have been effectively utilized as rheological modifiers, i.e. reducing self-consolidating concrete formwork pressure, extrusion, semi-flowable concrete for slipform paving, and 3D concrete printing, will be presented. Finally, some thoughts on potential directions for future work will be shared.

1. Introduction

The impacts of clay on cement-based materials have been studied for many years. Traditionally, clay is considered to be a harmful impurity within concrete aggregates forcing many aggregate producers to wash their sands to satisfy requirements such as ASTM C33 [1]. One reason for removing clays from aggregates is that due to their high surface area, minerology, and/or charge, clay surfaces become a “sink” that consumes mixing water and chemical admixtures during concrete production. They have become of particular interest coinciding with the introduction of polycarboxylate, as clays have an ability to absorb polycarboxylate and other surfactants (i.e. defoamers), leading to decreased efficiency [2,3]. Furthermore, the clay deposited on the surfaces of aggregate particles may lead to a weak interfacial transition zone between the cement paste and aggregate, thus reducing concrete strength, durability, and wear resistance [4]. As deleterious clays within sands can fluctuate, issues with consistent slump and air would arise. The concrete industry has responded with chemical solutions including sacrificial agents, which preferentially adsorb on to clays to allow polycarboxylates and defoamers to remain effective [5–7], and by limiting the content of particles smaller than 75 μm in aggregates [1]. It should be noted that, alternatively, clays are beneficial for earthen (or soil-based) materials, where it is able to enhance cohesion and act as an effective binder. These systems can be further stabilized with the use of cement [8].

More recently, researchers have learned that when clay is processed into a finer-sized particle, some “adverse” effects of clays on concrete properties, such as the rapid reduction in flowability, could be garnered as a benefit for select casting applications. For example, the reduction in flowability resulting from the introduction of clays could improve layer adhesion of shotcrete, formwork pressure reduction of self-consolidating concrete, and buildability of 3D concrete printing if the clays are leveraged as mineral-based thixotropic admixtures. Furthermore, nanoclays, a subclass of clays with at least one dimension at the

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nanoscale, have been found to be particularly effective in modifying the fresh state properties of cement-based materials at modest rates, i.e. less than 1% by mass of binder.

Nanoclays (NCs) are nanoparticles often derived from natural clays, such as kaolin and montmorillonite clays, whose interlayers have been separated through mechanical shearing, thermal and/or chemical modifications [9,10]. Kaolin clay primarily consists of kaolinite minerals, which have a 1:1 layer structure (one tetrahedral and one octahedral layer) and the two layers are held together by van der Waals attractive forces and hydrogen bonds. Owing to the strength of the hydrogen bond, water cannot penetrate between the layers, and so kaolinite is generally non-swelling in water. Montmorillonite is a member of the diverse smectite group, and it has a 2:1 layer structure (two tetrahedral layers and one octahedral layer), and their outer layers are loosely held together by weak van der Waals forces and can be separated easily by the penetration and uptake of water molecules, leading to swelling. For this reason, nanosized montmorillonite is often chemically modified to become hydrophobic by cation exchange before being used in cement-based mixes, where water is present [11]. Another common NC is made of highly purified magnesium aluminosilicate particles, which are chemically exfoliated from bulk attapulgite to remove high water demand impurities such as bentonite and other swelling clays [12]. The clay mineral has a 2:1 layer, fibrous structure, and it contains various hydroxyl groups (such as Al–OH and Mg–OH), with oxygen ions on the tetrahedral sheet, water molecules coordinated to Mg ions at the edges or ends of the fibers, and Si-OH groups along the fiber axis [13]. Due to its unique fibrous structure and high specific surface area, attapulgite can retain water up to 200% of its own weight [9,14]. Under shearing, the NC particles break down into needle-like structures with an average length of 1.75 μm, an average diameter of 30 nm, and specific surface area of 150 m^2/g (compared to 0.3–0.4 m^2/g for ordinary Portland cement) [15]. Among all the NC types, attapulgite NC has been the most commonly investigated as a rheological modifier in cement and concrete. As they are manufactured by separating the interlayers of natural clays, NCs are generally believed to be easily dispersed under shearing by conventional mixing, and therefore require little to no pre-dispersion when used in concrete production. Additionally, because the raw materials originate from naturally occurring sources, NCs generally have advantages in terms of availability, cost, and handling safety over other nanomaterial types, such as nanosilica [16].

This paper provides an overview of the use of NC in cement-based materials, with a focus on tailoring the fresh state properties. First, the effect of NC on shear rheological properties, i.e. yield stress, viscosity, and thixotropy, will be discussed. This macroscale flow behavior will then be tied to the effect of NC on the fresh microstructure, which can be characterized via focused beam reflectance measurement and compressive rheology. This will provide insight on the mechanisms underlying the effect of NC on shear rheology through an improved understanding of their effect on flocculation and coagulation behavior. Although NCs have primarily been used as rheological modifiers, any secondary effects they have on the hardening and hardened properties of cement-based materials are necessary to understand. Therefore, this paper will also discuss the effect of NC on cement hydration, mechanical properties, shrinkage and durability. Finally, examples of casting applications in which NCs have been effectively utilized as thixotropy modifiers, i.e. reducing self-consolidating concrete (SCC) formwork pressure, extrusion, semi-flowable SCC for slipform paving, and 3D concrete printing, will be presented.

2. Effect on rheological properties

Clay suspensions are known to exhibit thixotropic properties, which is mainly attributed to the unlike charges on the surfaces of clay particles compared to their edges [17]. At rest, this gives rise to a "house of cards" effect, where edge to face interactions result in the formation of a network, which translates to an increase in yield stress [18]. And under steady state flow, the network progressively breaks down and the clay particles orient themselves so that their like surface charges align, resulting in a decrease in apparent viscosity. Cement-based suspensions are also inherently thixotropic, where degree of thixotropy can be described, for instance, by characteristic time (a few minutes for flocculation, a few seconds for deflocculation) [19]. Degree of thixotropy can be modified through a number of different ways, including the addition of clays. As their working mechanism is primarily tied to surface interactions, their effect can be enhanced when introduced in the modified, nano-sized form due to increased specific surface area and purity.

In general, NCs have been found to increase yield stress and viscosity when introduced into cement-based systems. Dajaeghere et al. investigated the effect of attapulgite NC (0.5 to 2.5% by mass) in mixes that incorporated fly ash and superplasticizers, and found that they increase dynamic and static yield stress and plastic viscosity [20]. This agrees with the observations of other clay types, including nano-bentonite and nano-sepiolite [21,22]. The increase in viscosity by attapulgite NC has also been tied to decreased sand migration as measured through rheometry [23], and segregation resistance of SCC as measured through visual inspection of slump flow tests [24]. It should be noted that although attapulgite NCs have been found to increase viscosity, they also lead to high shear thinning capacity, where viscosity decreases substantially under sustained shear [25] or higher shear rates [26] due to progressive separation and alignment of the NC particles in the direction of flow [27], and separation maintained by the electrical repulsion between charged surfaces. As a result, their influence on viscosity at a given strain rate can be less than their influence on static yield stress, as shown in Fig. 1a [25].

2.1. Structural build-up

Primarily considered to be a thixotropy modifier, there have been numerous studies on the effect of NC on the time evolution of rheological properties, namely structural build-up behavior. Due to the complex nature of cementitious materials, structural build-up is a function of both reversible structural changes from the thixotropic phenomena and irreversible structural changes due to hydration mechanisms [28]. In terms of methodology, structural build-up is generally referred to as the increase in the magnitude of rheological properties with time (i.e. viscosity increase vs yield stress increase) when no attempt is made to determine the mechanism causing the increase in the measured parameter. However, as the origin of structure of fresh cement pastes is tied to soft colloidal interactions (i.e. van der Waals and electrostatic interactions) and rigid interactions due to early hydration (e.g. calcium silicate hydrate (C-S-H) bridging) [29], investigating the effect of NC on structural build-up via shear rheology can provide some insight into their effect on these two interactions. Structural build-up has been characterized through a number of rheological methods, which will be discussed herein.

2.1.1. Yield stress evolution

The rate of yield stress increase over time is commonly taken to be a measure structural build-up behavior of cement-based materials [30], and can be described through a thixotropy parameter proposed by Ovarlez and Roussel, A_{thix}, which is the linear slope of the static yield stress versus time curve [31]. Generally, NCs have been found to enhance rate of yield stress increase to some degree [32], which has been tied to increases in both rate and cumulative heat of cement hydration [33–35]. This can be attributed to potential filler and/or seeding effects by the NC, which is commonly observed when incorporating nanomaterials in cement-based materials due to their fine size and high specific surface area [14,36]. However, Ma and Kawashima applied a modified version of YODEL, originally proposed by Flatt and Bowen [37] and modified by Lecompte and Perrot [38], which describes the

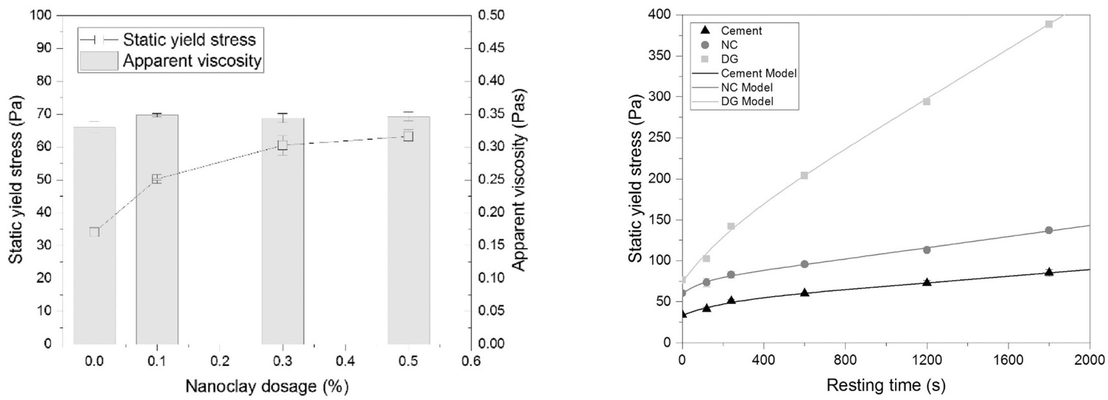

Fig. 1. a) Influence of attapulgite NC dosage on rheological parameters, showing an increase in static yield stress with little change in viscosity (under the same applied shear rate) at dosages up to 0.5% by mass of cement. b) Influence of 0.3% attapulgite NC on static yield stress evolution compared to neat (Cement) and 0.025% solid content of diutan gum by mass (DG), showing an immediate effect on static yield stress by NC (33.3 Pa vs 60.2 Pa for Cement and NC, respectively) but little over time (A_{thix} of 0.020 vs 0.034 for Cement and NC, respectively, and 0.151 for DG) [25].
[Reprinted with permissions from Ma et al. 2018 [25]].

dependence of yield stress on packing state and solid volume expansion due to cement hydration, to attapulgite NC-modified oil well cement pastes [26]. They found that the model was not able to fully capture the static yield stress evolution of NC-modified pastes, indicating that their effect on hydration may not be the only factor controlling structural build-up over time. Further, it has been shown that the primary increase in static yield stress exhibited by NC-modified mixes compared to the control is at the very beginning, i.e. immediately or very shortly after flow cessation, or when resting time equals zero [25,39,40], as shown in Fig. 1b. This indicates that the effect of attapulgite NC on structural build-up can be tied primarily to colloidal effects, which occurs a few seconds after flow cessation, versus hydration effects, which occurs over time [29]. Similar effects have been captured in viscosity evolution, where attapulgite NC increased initial viscosity but contributed little to the increase over time compared to the control [41].

2.1.2. Storage modulus evolution

As static yield stress is commonly characterized via flow onset, it is not possible to separate colloidal and hydration effects on A_{thix} due to the order of magnitude of the applied strain; flow onset is associated with a few % strain while the rigid network formed via hydrates is on the order of a few hundredths % strain [29]. Small amplitude oscillatory shear (SAOS), on the other hand, applies a shear amplitude on the order of a few hundredths % strain and so can probe the rigid microstructure tied to the formation of early hydrates between cement particles. Conflicting results have been found when quantifying structural build-up via SAOS, where in some cases attapulgite NC were found to decrease storage modulus compared to the control [25] while others have found that attapulgite NC-modified paste initially exhibits higher storage modulus compared to the control paste but is then surpassed over time, potentially indicating interactions with the formation of ettringite [42,43]. Moeini et al. found that depending on the NC type, storage modulus either increased or decreased compared to the control [44]. In general, the effect of NC on storage modulus evolution has been less investigated compared to their effect on static yield stress evolution, and the few studies that have investigated both storage modulus evolution and yield stress evolution indicate they do not necessarily exhibit the same trends of structural build-up [25,44]. Thus more SAOS investigation is needed to further elucidate the effect of NC on colloidal versus hydration effects on structural build-up, and to better understand the discrepancies observed in storage modulus evolution results.

2.1.3. Other methods of evaluating thixotropy

It is worth noting that there have been other methods applied to evaluate the effect of NC on structural breakdown and build-up behavior. The hysteresis loop has been used to quantify the degree of thixotropy of cement-based systems [28,45]. In its most general sense this consists of a protocol in which the shear rate is ramped up and then ramped down, and the area between the curves in the resultant shear stress-shear rate diagram is called the hysteresis area. Attapulgite NC has been found to increase the hysteresis area, indicating increased structural breakdown and structural build-up [46]. However, Yuan et al. found that the trends between hysteresis loop and yield stress evolution did not necessarily agree [35]. So although a quick method of analysis, it is difficult to clearly separate structural breakdown and build-up behavior using this technique since the shear rate is applied as a linear ramp up and down and steady state is not achieved.

Kawashima et al. used a breakdown-recovery protocol where paste is initially broken down at a constant shear rate and then a constant stress, which is below the yield stress of the material, is applied while the rate of shear rate decay is recorded and taken to be a measure of structural build-up kinetics [43]. Results indicated that attapulgite NC can significantly accelerate rate of rebuilding, where the characteristic time was reduced by an order of magnitude. Conte and Chaouche implemented large amplitude oscillatory shear (LAOS) to characterize thixotropy and deduced that the same NC type increased yield stress, indicated by the increase in moduli and extension of the linear viscoelastic regime, and enhanced shear thinning [42]. Qian and De Schutter quantified thixotropy through the difference between initial and equilibrium torque as measured under a constant shear rate, shown in Fig. 2a, which are associated with static and dynamic yield stress, respectively [47]. This was termed as the thixotropic index, where a higher value indicates higher level of thixotropy, and they found attapulgite NC to enhance thixotropy with and without the incorporation of PCE, as shown in Fig. 2b. Panda et al. employed a protocol of intermediate (0.1 s^{-1}), high (300 s^{-1}), then intermediate applied shear to measure shear thinning and viscosity recovery, and found attapulgite NC brought a faster rate of viscosity recovery in high volume fly ash mixes [39].

2.1.4. Structural build-up under applied stress at rest

Studies on the effect of NC on structural build-up are expected to increase with the continued interest in 3D concrete printing, where the viscoelastic behavior after placement becomes particularly important, as it will determine deformation, layer stability and buckling stability [48]. In characterizing structural build-up, it should be considered that printed layers will be subjected to self-weight and the weight of subsequently placed layers, in contrast to conventional casting where support is provided by the formwork [31]. Therefore, understanding the role of applied stress at rest on structural build-up behavior will become

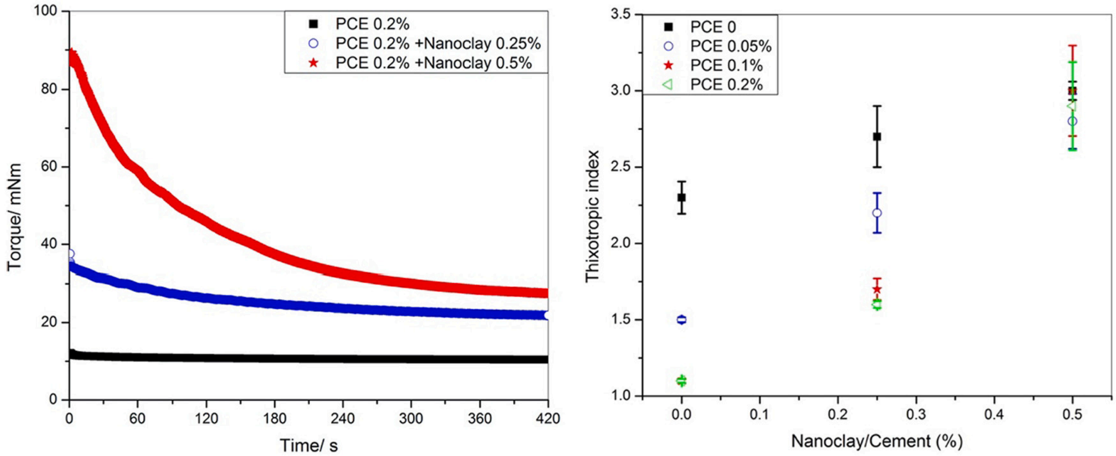

Fig. 2. a) Torque decay and b) plot of thixotropic index (thixotropic index = initial torque – equilibrium torque) of cement pastes with polycarboxylate ether superplasticizer and attapulgite NC addition. Results indicate that NC increases initial torque (i.e. static yield stress) more than equilibrium torque (i.e. dynamic yield stress), which leads to an increase in thixotropic index. This is observed in pastes with PCE additions up to 0.2% by mass of cement.
[Reprinted with permission from Qian and Schutter 2018 [47]].

critically important for applications like 3D concrete printing. Although the presence of residual stress after flow cessation has been well studied in colloidal suspensions and glassy systems, it has not been studied extensively for cement-based systems, with a few exceptions [49,50]. Ma and Kawashima investigated the effect of applied stresses at rest on the structural build-up behavior of neat cement pastes and found an accelerating effect on rate of yield stress increase overall, which was attributed to an elongated elastic limit associated with early hydration products between cement grains and resultant rigidification [51]. In contrast, attapulgite NC-modified pastes were insensitive to applied stresses at rest, where the protocol and results are shown in Fig. 3a and b, respectively. This was attributed to the fact that the system resembled a thixotropic clay system, which can be independent of applied stress in the solid state [52]. Conte and Chaouche investigated the same behavior

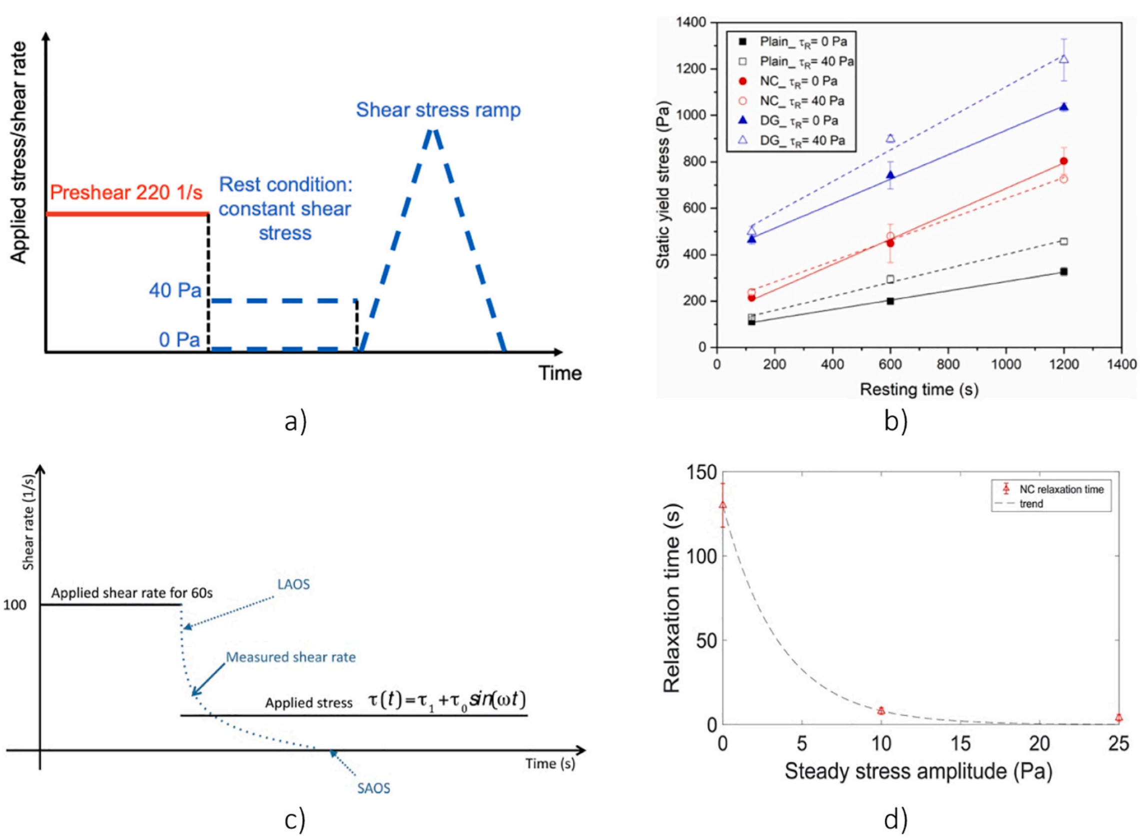

Fig. 3. Shear rheological protocols (a and c) and corresponding structural build-up responses under applied stress at rest (b and d). b) Static yield stress evolution of attapulgite NC-modified paste compared to plain and diutan gum-modified pastes, showing the NC-modified paste is not affected by an applied stress at rest of 40 Pa [51]. d) Relaxation time as a function of applied stress for attapulgite NC-modified paste, showing decrease in relaxation time (i.e. increase in structural build-up kinetics) with increasing applied stress at rest [53].
[Reprinted with permission from Ma and Kawashima 2020 [51] and Conte and Chaouche 2019 [53]].

but through superposition rheology, where oscillatory shear is superimposed to steady shear rate or stress to measure the evolution of the fresh microstructure under stress, as shown in Fig. 3c [53]. They found that rebuilding kinetics accelerated with stress amplitude, including for pastes modified with attapulgite NC, as shown in Fig. 3d. The protocols were quite different between the two studies, and further research is needed to better understand this phenomenon.

In summary, shear rheological studies thus far have focused on characterizing structural build-up via static yield stress evolution, and results support that NCs have an enhancing effect. However, more data is needed on the effect of NCs on structural build-up as characterized via storage modulus evolution, as results in the literature are currently contradictory. Further, for the application of 3D concrete printing, the role of internal stress at rest on the effect of NCs on structural build-up behavior should investigated. Studying this behavior can also help to fill a current knowledge gap, where the presence of residual stress after flow cessation has not been extensively studied in cement-based materials, in general.

3. Effect on fresh microstructure

Thus far the influence of NC on macroscale flow behavior (i.e. yield stress and viscosity) and elasticity (i.e. storage modulus) of fresh cement-based systems has been discussed. Although shear rheology can provide some insight into what is happening in the fresh microstructure by probing it at specified strain amplitudes and strain rates while measuring the corresponding response, it alone is not sufficient to fully understand how the NC is interacting within a cement suspension. There have been other methods of characterization to measure the agglomeration and flocculation behavior of NC-modified cement pastes that can help support what is observed via shear rheology.

3.1. Focused beam reflectance measurement

Agglomeration (flocculation accompanied by permanent coagulation) and dispersion of cement particles describe the physical processes occurring in the fresh microstructure of cement-based materials, including those that incorporate NC. When cement is mixed with water, a suspension is formed where the pore solution represents the continuous phase while particulates including any powder additions (e.g. NC) represent the dispersed phase. Within this suspension, a series of physiochemical reactions occur that result in the dissolution of cement phases and the formation of a three-dimensional network structure due to linkages among solid phases. This three-dimensional network will be responsible for responding to and resisting the shear-induced forces during mixing, placement and other fresh state processing procedures (e.g., pumping, finishing). As such, the formation and disruption of flocs within the network structure will affect the rheology of the paste and overall concrete. Intuitively, it can be understood that if the links among the flocs are weak and/or if the flocs take a long time to rebuild after being disrupted, then the viscosity and yield stress of the paste will be reduced. While the formation of the network structure is due to early hydration reactions, relatively little heat is given off during the time period of interest (i.e. mixing, pumping, placement). Thus, it can be very challenging to use calorimetric type methods to monitor the changes in the physical state of the system. Likewise, penetration type methods used to monitor setting are also not sensitive enough to detect the changes during this period. Additional challenges arise in fresh state microstructural characterization of the paste matrix since it is an aging, concentrated suspension containing polysized particles. Moreover, the high solid volume concentration and opacity limits the use of experimental methods that can be otherwise used to directly characterize suspensions. However, Ferron et al. has shown that laser back-scattering approaches, such as those employed in the focused beam reflectance measurement (FBRM), described in Fig. 4a and b [54,55], can be used to quantitatively assess the flocculation state occurring within cement paste microstructure under shear and at rest [54]. By relating the time duration that it takes a focused laser beam to scan across flocs, the chord length of the floc and number of chords can be ascertained [56]. Thus, the technique can be used to gain a better understanding of *how* and *to what degree* changes in the microstructural network impact rheology.

Through the use of laser spectroscopy methods, such as FBRM, continuous monitoring of chord length develops statistics of the chord lengths, which results in the number distribution of the cement agglomerates' dimension: $n(d)$ where d is the chord length. Thus, the volume distribution can be determined as $y(d) = d^3 \cdot n(d)$, which multiplies the number distribution by the chord length to the cube, to evaluate the degree of agglomeration quantitatively. It has been shown that a lognormal-distribution regression can successfully represent the volume distribution of cement agglomerates, as well as shear-rate dependence on their median size [58,59]. The effect of admixtures on the microstructure has also been investigated. The use of cement dispersants, such as a polycarboxylate, enhanced cement dispersion, and a higher probability (or counts per a single laser probing) in the number distribution was revealed at a lower chord length [57,60,61]. By contrast, many flocculants, including NC, shifted the peak toward a higher chord length [54,62,63]. In a study comparing the cement paste containing a cellulose-based viscosity-modifying agent (VMA) with cement pastes containing clays, Ferron et al. showed that the state of flocculation differed when clays were used versus the VMA (see Fig. 4c) [54]. No changes in the degree of flocculation were seen in the VMA adjuvated pastes with respect to the control paste. However, in pastes containing a

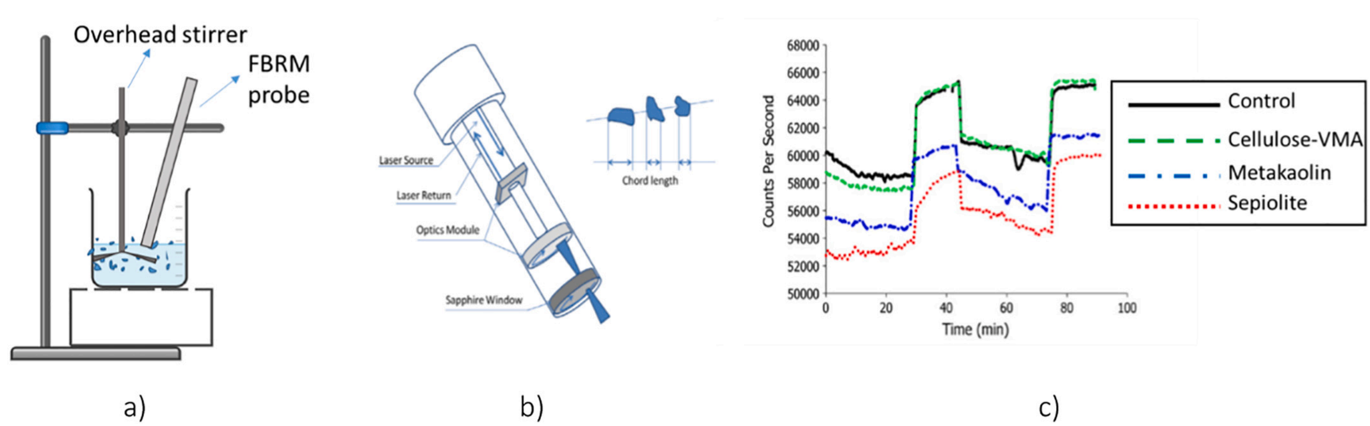

Fig. 4. Application of FBRM. (a) Schematic of FBRM probe conducting measurements in suspension during mixing; (b) operation mechanism for FBRM probe for chord length measurement; and (c) number of chords determined via FBRM for control paste, pastes containing clays, and paste containing a VMA.
[Panel b is reprinted with permission from Han and Ferron 2015 [57]. Panel c is adopted from Ferron et al. 2013 [54]].

metakaolin or sepiolite clay a significant increase in the degree of flocculation occurred, thus showing that while both VMAs and clays can increase rheological properties, the mechanisms governing the rheological changes differs. Similar conclusions were drawn in a shear rheological study that compared the yield stress and storage modulus evolution of diutan gum versus attapulgite NC [25]. Both the strain associated with the static yield stress and storage modulus of diutan gum-modified versus attapulgite NC-modified pastes were found to be orders of magnitude different (approx. 0.7 vs 0.05 and a few 10^2 vs 10^4 Pa, respectively) indicating the different working mechanisms of the two admixtures, although both led to increases in yield stress evolution compared to the control (shown in Fig. 1b).

Various mechanisms contribute to increasing the microstructural flocculation state when clays are employed, including particle packing effects [41,64], water or polycarboxylate adsorption [46,47], and electrostatic attraction [46]. Particle packing effects [41,64], such as shape and size distribution of clay, will also play a role as they impact packing density and interparticle distance. Regardless of the exact mechanism governing the increase in flocculation of pastes containing clays, this increase in flocculation can be correlated to an increase in rheological properties such as viscosity and yield stress [32,64,65]. This is in good agreement with work that showed that systems containing clays result in flocs that are more resilient and less sensitive to dynamic disturbances [54]. Additionally, Pignon et al. determined that beyond a critical volume fraction of clay in clay-water suspensions, a transition occurs that increases the bond strength of the network structure [66]. While studies thus far support that there are clear ties that can be made between the agglomeration behavior measured via laser back-scattering methods and shear rheology, additional work is needed to elucidate the linkage between them.

3.2. Consolidation behavior

The effects of NCs have also been quantified through constrained one-dimensional compression. Analogous to a shear yield stress, there is also a critical stress representing the onset of consolidation. When an applied stress exceeds this value, the microstructure of the suspension will collapse and rearrange to a denser configuration. During this process, the fluid within the flocs will be released and migrate out of the microstructure. The resulting configuration will be denser with more contact points between flocs and particles (i.e. higher local volume fraction) and thus will be more difficult to rearrange, leading irreversibly to a higher critical consolidation stress as a result of tighter flocs manifesting itself in a floc strength. Below this critical stress, the microstructure will respond elastically.

A common way to quantify the critical consolidation stress is through a centrifugal approach by Buscall and White [67]. An increasing series of accelerations can be applied to a cement suspension, where at each acceleration level an equilibrium height of the sediment is measured. Based on force balance and continuity considerations, Eq. (1) can be solved for both the critical yield stress and local solids volume fraction:

$$\frac{dP}{dz} = -\Delta\rho g \varnothing_0 \left(1 - \frac{z}{R}\right), \tag{1}$$

where P is the pressure, z is the distance from the bottom of the centrifuge specimen tube, $\Delta\rho$ is the density difference between solid and liquid phases, g is the centrifugal acceleration, ϕ_0 is the initial volume fraction, and R is the distance between the center of rotation and the bottom of cement suspension. To solve this differential equation, approximations have been developed by Green et al., shown in Eqs. (2) and (3), which calculate the pressure and volume fraction at the bottom of the cement suspension, respectively [68].

$$P(bottom) \cong \Delta\rho \varnothing_0 H_0 g \left(1 - \frac{H_{eq}}{2R}\right), \tag{2}$$

$$\varnothing(bottom) \cong \frac{\varnothing_0 H_0 \left[1 - \frac{1}{2R}\left(H_{eq} + g\frac{dH_{eq}}{dg}\right)\right]}{\left[\left(H_{eq} + g\frac{dH_{eq}}{dg}\right)\left(1 - \frac{H_{eq}}{R}\right) + \frac{H_{eq}^2}{2R}\right]}, \tag{3}$$

where H_0 is the initial height of the cement suspension and H_{eq} is the equilibrium height of the sediment at an acceleration level. $P(bottom)$, the critical consolidation stress at the bottom of the suspension, can then be plotted as a function of $\phi(bottom)$, the local volume fraction at the bottom of the suspension, for a series of equilibrium heights corresponding to different acceleration levels.

In Tregger et al., this method was used to evaluate the effects of three different clays on the consolidation behavior of cementitious systems [64]. Of the three clays (C1, C2, C3), C1 was attapulgite NC and the other two clays were a kaolinite and metakaolinite with dimensions on the order of a few microns. Fig. 5 compares the critical consolidation stress as a function of the local volume fraction as computed by Eqs. (2) and (3) for each of the clay systems along with a reference without clay. Each of the clays were dosed at 1% solids/cement (s/c). For each set of data, a simple regression was performed to fit the data to an equation of the form:

$$P = a \times exp(b(\phi - 0.45)) + c, \tag{4}$$

where P is the critical stress, ϕ is the local volume fraction and a, b, c are fitting parameters.

In this form of the equation, b represents a relative proxy for the increase in the resistance to consolidation of the suspension as the local volume fraction increases. C1 exhibited the highest b value, which may suggest that with C1 a stiffer suspension is achieved. Fig. 6 shows this b value, a consolidation factor, plotted against the shear yield stress as obtained by a flow curve. C1 is shown to have a higher consolidation factor, as well as a higher shear yield stress, while C2 and C3 show only small increases in the consolidation factor. These results indicate that NC led to a significant increase in floc strength, which agrees with the results of shear rheology, i.e. increased yield stress and viscosity, and FBRM, i.e. increased chord length, discussed prior.

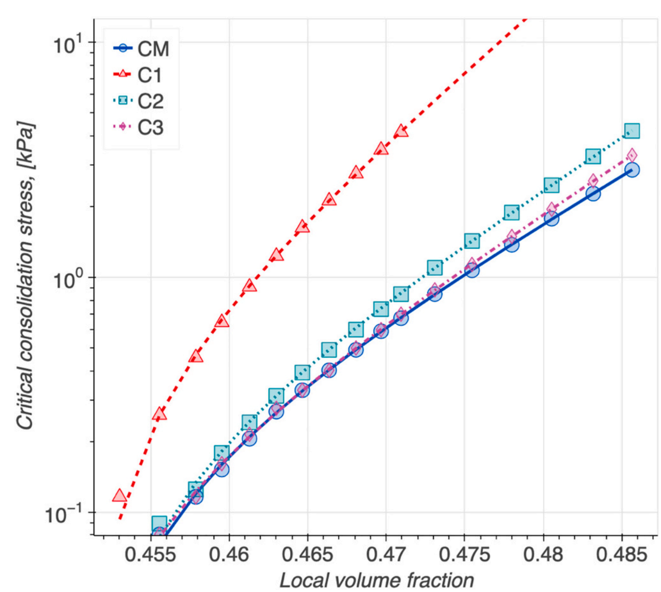

Fig. 5. Impact of clays on the consolidation behavior. CM – control; C1 – C3 are different clay types dosed at 1% solids/cement. [Adopted from Tregger et al. 2010 [64].].

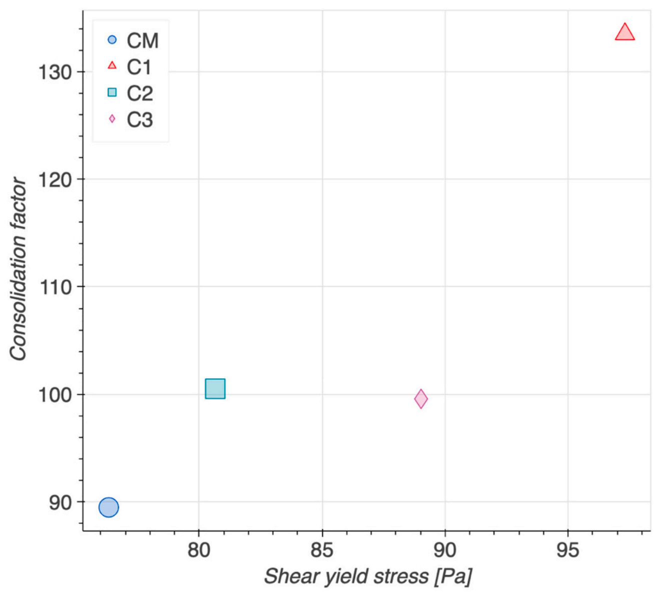

Fig. 6. Consolidation characteristics of cementitious systems containing clays. [Adopted from Tregger et al. 2010 [64]].

4. Effect on hardening and hardened properties

Although within the context of this paper NC is primarily viewed as a rheological modifier to facilitate casting, their effect on hydration, strength gain, shrinkage and durability are also important to consider for field application and will be discussed herein.

4.1. Hydration kinetics

Like many other nanomaterials, NC particles can act as nucleation sites for C-S-H growth during the cement hydration process, possess pozzolanic reactivity, and fill voids. All of these effects serve to densify the cement matrix with more C-S-H and less calcium hydroxide (CH), resulting in improved mechanical properties, thermal behavior, and microstructure of cement pastes and mortars [24,69]. Fig. 7 shows the effect of attapulgite NC on the hydration kinetics and strength development of a cement paste in comparison with nanosilica (NS) and nanolimestone (NL) [70]. Fig. 7a–c show that all the nanoparticles studied accelerated cement hydration. This can largely be attributed to their nucleation effect, which resultantly enhances C-S-H precipitation, accelerates the hydration rate of C_3S, and shortens the induction period. NS and NL influenced the silicate peak the most, which is mainly related to the hydration of calcium silicates (C_3S and C_2S) (Fig. 7 a and b). In contrast, NC particles significantly increased the aluminate heat peak, which is mainly related to secondary hydration of C_3A, as the aluminates from the NC can alter the sulfate-aluminate balance [71]. The times for the cement pastes containing NC to reach the silicate and aluminate peaks of heat flow were also significantly shortened. Other studies have also found similar accelerating effects by atttapulgite NC [26,34].

4.2. Strength gain

Fig. 7d–f reveal that like NS and NL, 1% attapulgite NC increased the compressive strength of cement paste at 3 and 7 days. The strength improvements can partially be attributed to accelerated cement hydration by the nanoparticles. Moreover, as the nanoparticles are well dispersed in the cementitious system, C-S-H nucleation and production can take place in the voids between cement grains, which makes the cementitious matrix more homogeneous and denser. Furthermore, the aluminates, which are richer in the pore solution of the NC-modified

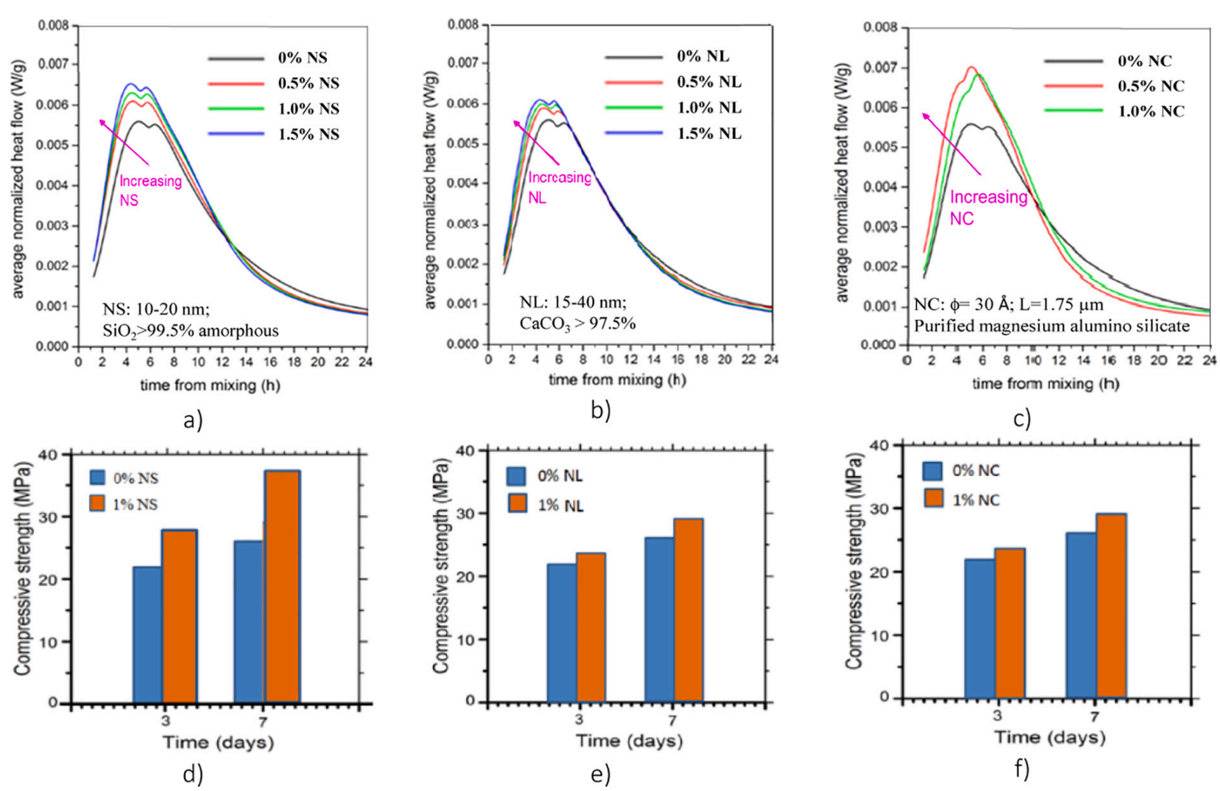

Fig. 7. Effects of attapulgite NC on cement hydration (a–c) and strength gain (d–f) in comparison with those of NS and NL at up to 1.5% replacement of cement by mass. Cement pastes were composed of 70% ordinary Portland cement, 30% Class F fly ash, and a water-to-binder ratio (w/b) of 0.5 [panels a–c were adopted from Wang et al. 2014 [70]. Panels d–f are unpublished results of Dr. Xin Wang and Dr. Kejin Wang.]

cement paste, can substitute silicon or calcium in C-S-H to form C-(A)-S-H gel, and this substitution creates a complex 3-D bonding scheme that may provide additional strength enhancement [72].

However, conflicting results have been reported on the strength improvement of NC-modified cement-based materials at later ages, especially those containing higher NC contents [20,73,74]. This may partially be attributed to the reduced degree of C_3S/C_2S hydration at later ages, as mentioned above. Another reason may be related to the dispersion of the NC particles, which generally becomes more challenging at high contents. Although NC is believed to be readily dispersible, research has found that sonication could significantly enhance their effect on concrete properties when compared to those of as-received NC due to improved dispersion [75]. Depending upon the size and amount, NC agglomerates could serve as weak points in the cement matrix, thus increasing porosity and reducing strength. Table 1 presents some experimental data on mortar mixes modified with attapulgite NC, published by Dejaeghere et al. [20] Their results illustrate that most mixes containing 2.5% attapulgite NC displayed a lower heat of hydration at 1 and 3 days than those containing 0.5%, indicating a reduced degree of cement hydration in the former. The table also shows that most mixes containing 2.5% NC had higher strength at 1 day but lower strength at 28 days than those containing 0.5% NC. In addition, the densities of mortar mixes containing 2.5% NC were generally lower than those of mixes containing 0.5% NC, implying that more pores may exist in the former. The existence of threshold levels have been observed in rheological studies, as well – Quanji et al. found that the rate of structural rebuilding increased compared to the control mixture when low dosages of attapulgite NC were used, but that additions over 1.3% led to a decrease [46]. Several other studies have shown that the use of NC slightly increased the amount of coarse capillary pores in cement paste [76]. According to Mota et al., higher alkali content can also lead to a higher capillary porosity at a given degree of hydration [77]. Moreover, if a cementitious system has a low pH value (7.5–12), the presence of sufficient magnesium by NC could destabilize C-S-H and form stable M-S-H, thus reducing strength at later ages [78].

Aside from attapulgite NC, the effect of other types of NC on the mechanical properties of cement-based materials have been reported by many researchers. It should be noted that in these studies, the focus was on the use of NC in improving the hardened properties and less so on their use as rheological modifiers. Morsy et al. studied the influence of metakaolin NC prepared from the thermal activation of kaolin clay, and found that the 28 day compressive and tensile strengths of mortars were improved by 7% and 49%, respectively, at 8% cement replacement [79]. Farzadnia et al. reported that the incorporation of 3% halloysite NC into cement mortars increased the 28 day compressive strength by 24% [80]. Hakamy et al. investigated the influence of NC derived from calcined and non-calcined montmorillonite on the mechanical and thermal properties of cement paste [81]. They found that the NC significantly improved various mechanical properties of cement paste, including compressive, flexural, and impact strength, fracture toughness, hardness and thermal stability. The cement paste with calcined NC performed better than corresponding pastes with the non-calcined NC due to its pozzolanic reactivity, which in turn reduced porosity and water absorption of the cement paste. Fan et al. and Guo et al. found that kaolinite NC replacement of cement increased both compressive and flexural strength of cement mortar, and the improvement was more significant on flexural strength than on compressive strength [82,83]. In brief, the effects of NCs on cement hydration kinetics and strength development depend not only on their particle sizes, which control the nucleation effect, but also their mineral and chemical characteristics.

4.3. Shrinkage behavior

One of the unique properties of clay materials is its plasticity. Plasticity is a property that allows the material to permanently deform without fracturing. In a clay paste, the water that surrounds the clay particles and makes a clay paste workable, which is generally up to 20–35% by mass of the clay paste, is typically referred to as the *water of plasticity*. As shown in Fig. 8, when the water of plasticity evaporates, the clay particles move closer together, causing the clay paste to shrink. During this stage, the volume change due to the shrinkage of the clay paste is linearly proportional to the volume of evaporated water. Once the clay particles are in contact with each other, the clay paste becomes rigid and the volume change of the clay paste begins to stop, although

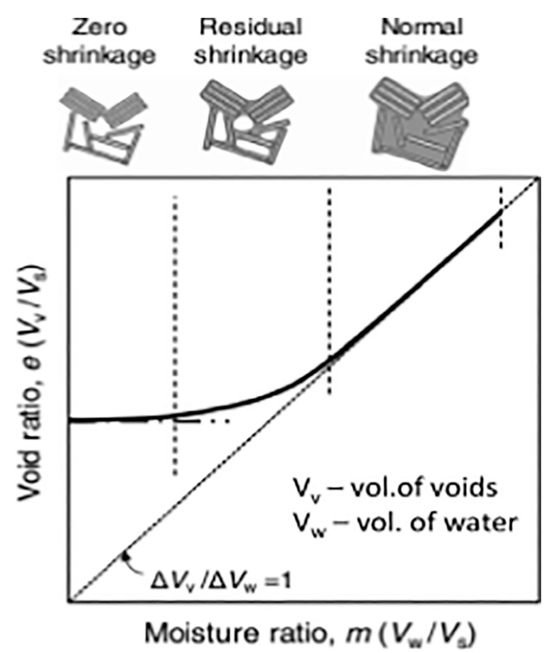

Fig. 8. Clay shrinkage curve. V_s is solid volume.
[Reprinted with permission from Lu and Dong 2017 [84]].

Table 1
Properties of mortar containing different amount of attapulgite NC.

Mix	Mortar [%]			Density	Heat of hydration [W/kg]		Compressive strength [MPa]			
	NC	SP	FA	[g/cm^3]	1d	3d	1d	3d	7d	28d
1	0.5	0.6	5	2.13	1.184	0.256	22.5	49.3	61.8	73.6
2	2.5	0.6	5	1.97	0.859	0.250	26.4	40.2	46.9	66.7
3	0.5	3.0	5	2.16	1.936	0.283	9.2	47.4	69.6	83.1
4	2.5	3.0	5	2.18	1.876	0.272	15.6	46.3	60.0	75.0
5	0.5	0.6	20	2.13	1.274	0.210	22.8	50.1	55.0	77.7
6	2.5	0.6	20	2.05	0.875	0.206	19.8	34.2	45.0	54.5
7	0.5	3.0	20	2.16	0.909	0.262	5.6	44.2	57.3	75.4
8	2.5	3.0	20	2.11	0.973	0.245	12.9	42.7	61.7	73.1

Note: The mortar had a sand volume of 30% and a w/b of 0.40.
[Adopted from Dejaeghere et al. [20]].

the water remaining in the pores continues to evaporate. Shortly, a minimum clay paste volume, called the shrinkage limit, is reached, and pores form in the clay paste [84]. It should be noted that the clay shrinkage behavior illustrated in Fig. 8 describes the behavior of bulk wet clay pastes. Similar phenomenon may happen if NC particles are agglomerated in cement-based materials, leading to increase in shrinkage and generation of more coarse voids. Nevertheless, if NC particles are well dispersed, the degree of shrinkage will depend upon the surface water absorption of the NC particles and the availability of free water in the cement-based material, and the generation of coarse voids by NC particles under drying as depicted in Fig. 8 would be minimal.

Gao et al. investigated the effect of three different clays, C1 – attapulgite (150 m^2/g), C2 – kaolinite, illite and silica (23 m^2/g), and C3 – metakaolin (13 m^2/g), at an addition of 2% by mass of binder on the autogenous, free drying, and restrained shrinkage behavior of a self-consolidating mortar (Fig. 9) [15]. C1 and C2 were NC, where one dimension was at the nanoscale, while C3 was at the micron scale. It was found that C1 and C3 increased autogenous shrinkage while C2 increased autogenous shrinkage during the first 5 days but slightly reduced it at later ages compared to the control (Fig. 9a). The mortar containing C1 was also found to exhibit the highest drying shrinkage, followed by the mortar with C2 then the mortar with C3. This trend was consistent with that of the specific surface areas of the clays, which infers that drying shrinkage was largely due to the adsorption of surface water on the clay particles. The influence of finer particles on cement hydration and microstructure development may have also contributed to the drying shrinkage behavior, thus leading to the lowest drying shrinkage of the mortar with C3. Restrained shrinkage was measured via the restrained ring test under unsealed conditions, and the recorded strain development and cracking behavior are the result of a combined effect of total shrinkage, strength, and creep behavior. Fig. 9c shows that all three clays increased strain and led to earlier cracking of the mortar. Focusing on the attapulgite NC, C1, it was discussed prior that at higher dosages (e.g. 2% used in this study) dispersion may become an issue, which can hinder strength development and exacerbate shrinkage due to aggregation of the NC particles and resultant coarse voids in the cement matrix.

Lomboy et al. studied the shrinkage and fracture behavior of self-consolidating mixes similar to those studied by Gao et al. but with only 0.5% attapulgite NC addition [85]. In contrast, they found that at this lower addition level attapulgite NC slightly reduced free drying shrinkage and consequently postponed the cracking time of the concrete under restrained, unsealed conditions. Similarly, Lee et al. studied the plastic shrinkage behavior of concrete containing 0.25% organo-modified montmorillonite NC and found that it exhibited significantly reduced plastic shrinkage compared to the control [86].

The existing literature indicates that lower additions of NC ($<$ 0.5%) can have minimal effect on concrete shrinkage and cracking potential. However, they can have adverse effects at higher addition levels ($>$2%), likely due to dispersion issues. Therefore more investigation is needed to evaluate shrinkage and shrinkage cracking before higher contents of NC are used in field concrete.

4.4. Durability

Durability of concrete is primarily dominated by its permeability, which is in turn governed by the pore structure of the concrete. Fan et al. and Guo et al. investigated the influence of nano-kaolinite clay (NKC) content on the pore structure of cement paste and chloride permeability of mortar [82,83]. Both research groups showed that cement replacement with NKC refined the pore structure of cement pastes, and subsequently limited the penetration of chloride ions. Zhang et al. also reported that a cement mortar mix showed reduced porosity when 1 and 2% metakaolin NC were used as cement replacement, but the porosity increased and pore structure became coarser when 3% was used [76].

Further, Fan et al. revealed that the use of NKC could improve freeze-thaw (F–T) resistance of concrete [87]. As shown in Fig. 10a, concrete mixes containing 1–5% NKC all had a higher value of relative dynamic modulus of elasticity (RDM) than the corresponding concrete mixes without NKC after 125 F–T cycles. In particular, 3% NKC led to the most enhanced concrete F-T durability, indicated by the highest RDM compared to the control. Zhang et al. also reported that addition of 1% metakaolin NC improved the F-T resistance of mortar [76]. Lomboy and Wang attested that with good air entrainment, SCCF concrete containing 1% attapulgite NC showed comparable F-T resistance to conventional pavement concrete after 300 F-T cycles [88]. Recently, Zhang et al. studied the effect of NKC on corrosion resistance of reinforced concrete [89]. As seen in Fig. 10b, when compared with the specimens with no NKC, the specimens with 1%, 3%, and 5% NKC reduced the rebar corrosion ratio by 22%, 47%, and 52%, respectively, after applying an electrical current for 36 h. They attributed the corrosion resistance to the densified concrete microstructure provided by the NKC.

In summary, the existing literature shows that the use of NC generally improves overall concrete durability. However, studies on the effect of various types of NCs on the broad range of durability properties, such as F-T, corrosion, alkali-silica reaction, and sulfate resistances, are still very limited. As the application of NC in concrete is gaining increasing attention, further extended and in-depth studies are necessary.

5. Applications

NC has been found to be effective in facilitating casting in a number of different applications, which will be described herein through case studies. Specifically, these case studies, both lab and field-based, show the potential of NC in serving as an effective thixotropy modifier to improve existing casting approaches, e.g. SCC formwork casting and slipform paving, as well as facilitate new ones, e.g. extrusion and 3D

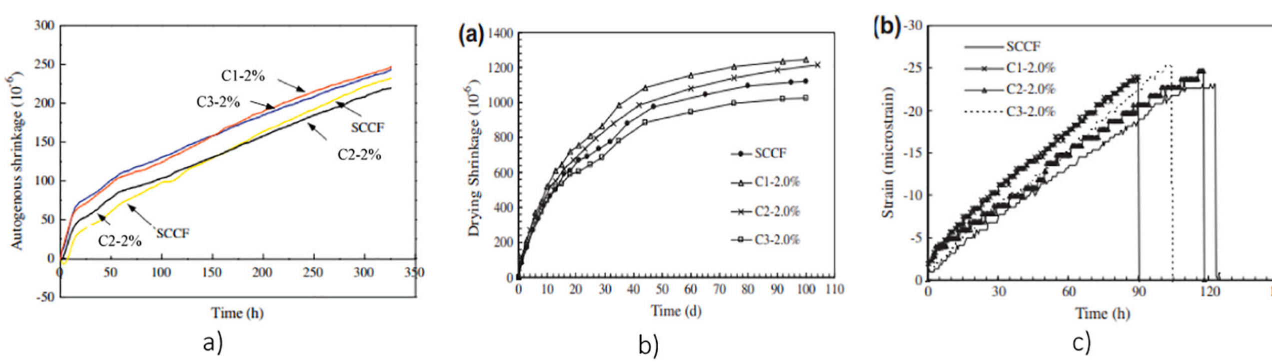

Fig. 9. Effects of NCs on a) autogenous, b) free drying, and c) restrained shrinkage of mortar.
[Reprinted with permission from Gao et al. [15]].

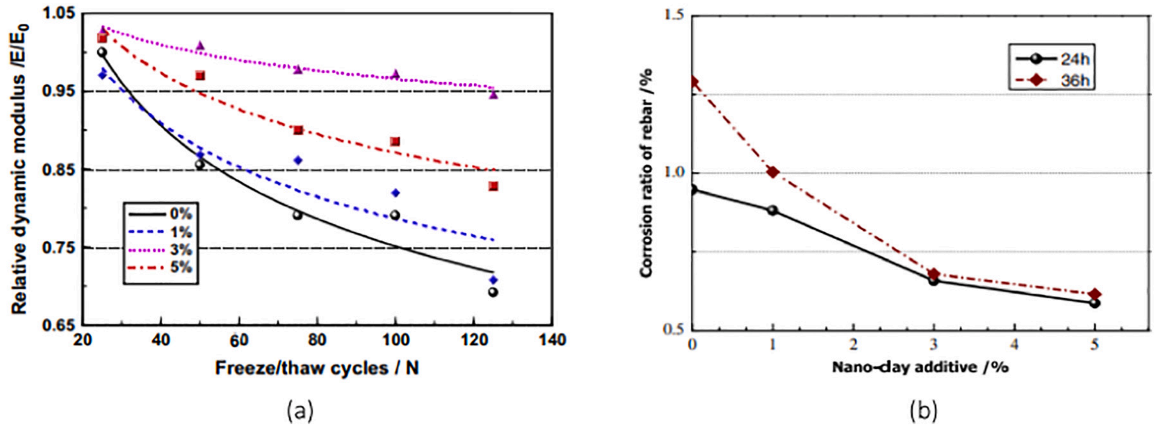

Fig. 10. Effect of NKC on a) freeze-thaw resistance [87] and b) corrosion resistance [89]. [Reprinted with permission from Fan et al. 2015 [87] and Zhang et al. 2021 [89].]

concrete printing. And they serve to motivate further study in the areas that were discussed earlier in this paper, to continue to improve understanding of the effect of NC on fresh and hardened properties, mixture proportioning, and NC selection and processing.

5.1. SCC formwork pressure

SCC can exert higher lateral pressure on formwork during casting due to the high flowability, or lower yield stress, and faster casting rates achieved with SCC compared to vibrated concrete. Enhancing the structural build-up of the fresh SCC mix, or increasing the rate of shear strength increase, can help reduce its formwork pressure by minimizing the transfer of vertical to lateral pressure. Various types of clays, including NC, have been found to be highly effective in doing so due to their thixotropic effect, while exhibiting sufficient shear thinning to reach the target flow properties of SCC [90,91]. In these studies, formwork pressure during casting was simulated in a lab environment using a pressure vessel, where a sample's pressure in the lateral direction was measured while a universal testing machine vertically applied a load onto it [92]. The applied vertical pressure increased up to 360 kPa (corresponding to 16 m concrete head) at 2 h. The lateral pressure exerted by SCC incorporating NC was the smallest among the samples incorporating various admixtures, such as silica fume and viscosity modifying admixtures. A simplified intrinsic two-function model [93], among others [31,94–97], was used to parameterize the test results. The self-weight (vertical pressure) of concrete, $\Delta p_V(t')$ applied at t', exerts formwork pressure over time ($t > t'$):

$$\Delta p(t,t') = \alpha(t,t')\beta(t')\Delta p_V(t') \quad (5)$$

where the pressure transfer separates into the delayed and instantaneous pressure-response functions, $\alpha(t,t')$ and $\beta(t')$, respectively. They could be simplified as:

$$\alpha(t,t') = 1 - a^2 t'(t - t') \quad (6)$$

$$\beta(t') = 1 - bt' \quad (7)$$

The instantaneous response linearly decreases with the loading time (t'), and a higher instantaneous coefficient (b) indicates a smaller formwork pressure. The delayed response decreases with a longer sustaining time ($t - t'$), as well as a longer loading time. The delayed coefficient (a) parameterizes it in the same manner as the instantaneous coefficient.

An SCC incorporating attapulgite NC at 0.33% per cement mass showed an instantaneous coefficient of b = 0.455 h^{-1} and a delayed coefficient of a = 0.145 h^{-1}. Another SCC produced by a different mix proportion, but the same dosage of NC, yielded coefficient values of b = 0.467 h^{-1} and a = 0.168 h^{-1}. The slump flows of both SCCs were within 590 and 630 mm. The coefficient values of the NC-modified SCC mixes were compared against those of several control SCC mixes with slump flows within the same range, and they exhibited coefficient values of b = 0.284 to 0.346 h^{-1} and a = 0.216 to 0.483 h^{-1}. NC had a clear effect on increasing the instantaneous coefficient, although not the delayed coefficient. This ties in with the rheological results of structural build-up, where they were found to have an immediate effect on build-up shortly after shear, and less so over time [25,41]. Further, it should be noted that the instantaneous coefficient is critical for formwork pressure development, while the delayed coefficient is less sensitive according to the model. Fig. 11 shows a simulation example for the formwork pressure development, where the mixes consider the pressure-response coefficients measured in the previous study [90,91].

5.2. Extrusion

The extrusion process involves forcing a material (which is usually pumped) through a die to create an extrudate with a desired shape and density. This requires a balanced rheology; stiff enough to retain shape

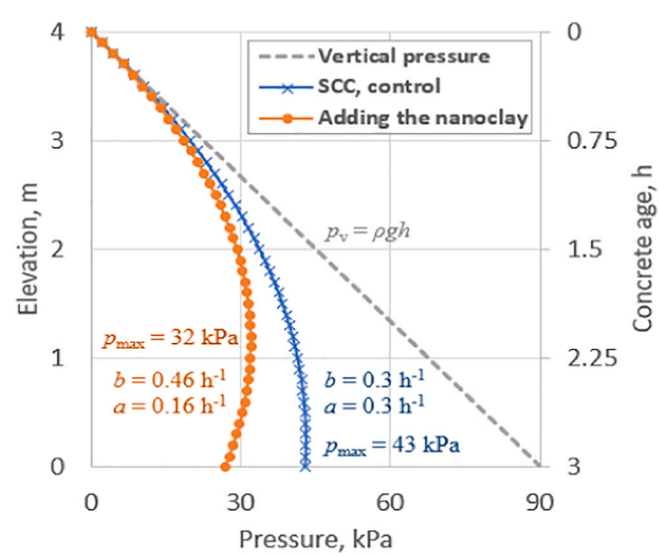

Fig. 11. Formwork pressure exerted by SCC. Placing a 4 m concrete wall for 3 h (casting rate R = 4/3 m/h) is simulated as an example, where the density of concrete is assumed as 2300 kg/m^3. Concrete age at each elevation is calculated by $t = h/R$, where h is the concrete head subtracting the elevation from the wall height. The formwork pressure is then obtained by $p(t) = wR(t\text{-}bt^2/2\text{-}a^2t^3/6 + ba^2t^4/12)$ for each mix.

after exiting the die but flowable enough to be extruded without tearing. Properly designed high-performance, fiber-reinforced cementitious composites (HPFRCC) can achieve this balance but typically require expensive processing aids such as cellulose ethers, preventing widespread adoption.

Kuder and Shah demonstrated the feasibility of clays to partially replace expensive processing aids while retaining the rheological balance required for extrusion [98]. Using a ram-extruder interfaced with a closed-loop hydraulic testing frame, the extrudability was observed for cementitious systems containing 14% Type I Portland cement, 33% fly ash, 12% silica fume, 39% water and 1% high-range water reducer (HRWR) by volume. In addition, one of two different cellulose ethers (hydroxypropyl methylcellulose, methylhydroxyethl cellulose) were used at dosages ranging from 0.5 to 2.0% solids by mass of binder. Additional mixtures were then tested where a portion of the cellulose ether was replaced by one of two different metakaolin clays – i) kaolinite, mica, and silica and ii) calcined kaolinite. Extrudability was evaluated as extrudates that did not exhibit phase migration, surface defects, or a high extrusion pressure during extrusion. Eighteen total tests were performed and it was shown that both cellulose ethers could be replaced up to 50% by a metakaolin while still maintaining extrudability.

In addition to evaluating the extrudability, the capillary rheology of the extrudate was tested by taking advantage of the interfaced closed-loop hydraulic testing frame. By recording the pressure required to extrude the material for a series of extruding velocities, flow curves could be created and processed to produce a yield stress and an equilibrium viscosity. Assuming laminar flow without slip at the walls, the apparent shear stress and shear rate can be given as:

$$\tau_{app} = \frac{PD}{4L} \tag{8}$$

$$\dot{\gamma}_{app} = \frac{8V}{D}, \tag{9}$$

where P is the extrusion pressure (kPa or psi), V is the mean extrudate velocity (mm/s or in/s), L is the capillary length (mm or in) and D is the capillary diameter (mm or in). In order to account for end effects, a correction using Bagley's approach was followed [99], which determines the true wall shear stress in the capillary, τ_w, by:

$$\tau_w = \frac{PD}{4(L+ND)}, \tag{10}$$

where N is the end correction factor for the imaginary extension of the capillary length.

Following this analysis, which was conducted over three different die lengths and six different extrusion velocities, flow curves were created and yield stress and viscosities were obtained. By plotting these values, it could be observed that extrudability is achieved within a defined yield stress and viscosity window as shown in Fig. 12. The color represents the clay content, while the size represents the amount of cellulose ether. It can be seen that replacement of the cellulose ethers with the clays (i.e. decreasing size) provided an increase in viscosity without detrimentally increasing the yield stress unless the dosing of clays was too high (3% solids on mass of binder). It is interesting to note that for higher yield stress materials to be successfully extruded, a higher viscosity is also required. It is postulated that with higher yield stress materials, a higher viscosity can help improve the cohesion of the material as it is extruded, leading to fewer tears and surface defects. However, there will be a limit as extrusion pressure increases with increases in the yield stress and viscosity.

5.3. Semi-flowable SCC for slipform paving

Another application of NC as a thixotropy modifier in SCC is for slipform paving. Modified with NC, conventional SCC can be semi-flowable, called semi-flowable SCC or SFSCC. SFSCC is designed to exhibit adequate flowability for self-consolidation and sufficient green strength to carry its self-weight and hold its shape right after casting. This SCC type allowed for external vibration to be eliminated during slip-form construction, thereby eliminating the issues associated with excessive consolidation [100,101].

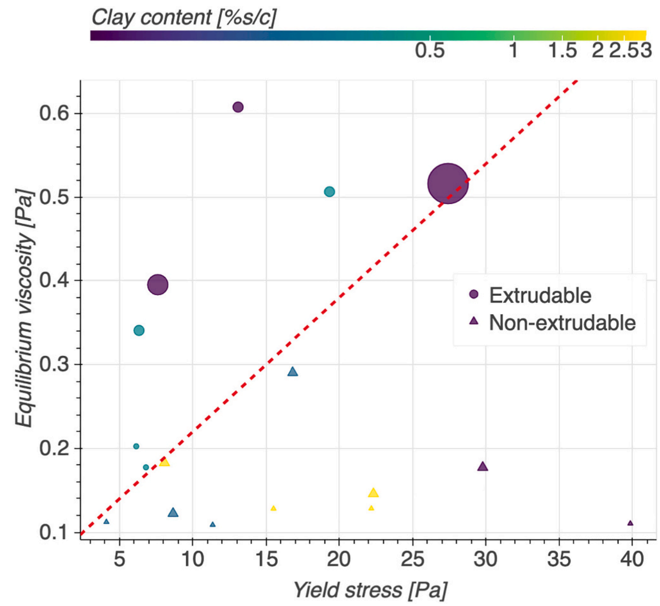

Fig. 12. Rheology conditions for successful extrusion. The color represents the clay content, while the size represents the amount of cellulose ether. [Adopted from Kuder and Shah 2007 [98]].

SFSCC with 1% attapulgite NC addition was utilized to construct a bike path pavement, where a 125 mm-thick SFSCC was placed on top of a 2.5 m wide and 18 m long old asphalt pavement in the City of Ames, Iowa, USA, in July 2008. The SFSCC mix proportion used is given in Table 2, where Type I cement, Class C fly ash, cellulose fiber (18 μm in diameter and 2.1 mm in length), attapulgite NC, and an air entraining agent were used. The coarse aggregate was crushed limestone with a nominal maximum size of 25 mm (size 57), and the fine aggregate was a #4 river sand.

All SFSCC materials were batched at a local ready-mix plant and mixed in a concrete mixing truck. The fiber and NC were first loaded into the concrete mixing truck, followed by the other materials. 15–20 min after mixing, the concrete mixture was delivered to the field site. Fresh SFSCC was tested for flowability and air content right before paving, and concrete samples were then cast at the field site. A modified asphalt paver with the auger and vibrators removed was used for slip-from paving without vibration (Fig. 13a). Two skids (125 mm high and 1.8 m long) were installed on each side of the paver to help the concrete mixture form a shape during paving. A dump truck was used to load the concrete mixture into the paver and to tow the paver forward. A person stood on the paver to spread the concrete mixture as the paver moved forward (Fig. 13b).

After paving was completed, a float and trowel were used to finish the SFSCC surface. Grooves were placed every 2.75 m as joint placement. The surface was then broomed for adequate surface texture. The curing method involved a plastic sheet covering a damp burlap for seven days. Table 3 presents the test results of the fresh and hardened SFSCC.

Field inspections performed after a winter season (March 2009) indicated that the SFSCC bike path showed only a very small area of very light scaling and that the overall pavement performed well. Although lab tests showed that addition of NC increased concrete drying shrinkage [102], no shrinkage cracks and other visible deterioration had been

Table 2
SFSCC mixture proportions with NC (kg/m^3).

Cement	Fly Ash	Water	River Sand	Limestone	AEA	Fiber	Nanoclay
332.1	143.9	183.8	727.5	860.1	230 ml/m^3	1.5	3.5

Fig. 13. a) Modified asphalt paver and b) slip form paving with SFSCC.

Table 3
Properties of SFSCC used for the slip form construction.

Property	Value
Slump, mm	178
Air content, %	8.75
28 day porosity, %	16.6
28 day rapid chloride permeability, coulomb	6322
Compressive strength, MPa	
7 days	26.6
28 days	35.0
56 days	36.5
Relative dynamic modulus of elasticity after 300 freeze-thaw cycles, %	82

observed in the bike path after approximately 3 years of field service. This case study demonstrated that NC can be used as a thixotropic agent to alter the rheological behavior of concrete to provide a timely balance between self-consolidation and shape-holding ability for SFSCC, to ultimately yield a pavement with good performance.

5.4. 3D concrete printing

Most recently, NC have been utilized as a thixotropy modifier to enable extrusion-based 3D concrete printing. In this process, it is desirable for a cement-based mix to exhibit a low yield stress to enable pumping and extrusion but then a rapid increase in yield stress immediately after deposition to achieve shape stability [103], similar to the performance described for extrusion and silpform paving. Given the effect of NC on cement rheology, i.e. shear thinning and rapid early structural buildup, it has been explored in a number of studies at additions up to 1% by mass of binder as a way to balance extrudability and shape stability, typically characterized via layer deformation, build height, and build rate of printed elements.

Bohuchval et al. utilized attapulgite NC and found that they improved extrudability and shape stability in mixes composed of fly ash, superplasticizers and sisal fibers [104]. Kazemian et al. found the same NC type to enhance shape stability, as measured through visible deformation of layers, and correlated this to increase in green strength, as measured through a fresh cylinder stability test [105]. Moeini et al. 2020 found similar effects on green strength but also found that the addition of NC can result in brittle failure [44]. Panda et al. also found attapulgite NC to increase green strength and stiffness, as measured through a fresh cylinder compression test; this translated to improved deformation resistance of printed layers and increased number of layers achieved during buildability tests [106]. Similar NC effects on buildability were observed in high volume fly ash mixes, as well [39]. However, it was also pointed out that accelerators would also be needed to tailor the rate of green strength development, which ties into the observation that NC have an immediate effect on yield stress but little on the rate of yield stress increase over time. Therefore, studies thus far demonstrate the advantages of NC, but also highlight that other admixtures are needed to address some of its limitations. Reales et al. found similar effects with a bentonite NC, although nanosilica was found to exhibit higher A_{thix} and subsequently higher maximum layer height and build rate [107]. This is likely tied to the enhanced seeding effect of nanosilica compared to that of NC, which can enhance hydration kinetics and, subsequently, structural build-up behavior over time. Studies have also found that attapulgite NC can increase yield stress while limiting workability loss [108,109], which can also be attributed to the effect of clays on immediate structural build-up after shear but not over time.

All in all, early lab studies show the potential of NC to tailor the fresh-state properties of 3D concrete printing mixes, namely during pumping and extrusion/deposition (Fig. 14), but more investigation is

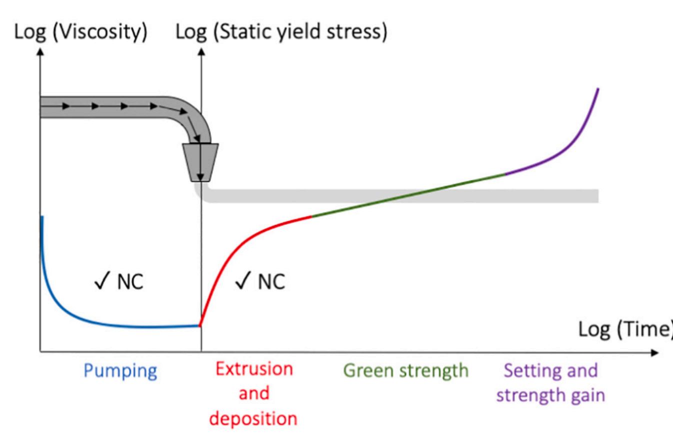

Fig. 14. Rheological requirements for extrusion-based 3D concrete printing. [Updated from Marchon et al. [103]] Early results have shown the potential of NC to facilitate the first two steps (i.e. pumping and extrusion/deposition) due to their effect on shear thinning and early structural buildup.

needed to develop mix design methodologies, i.e. NC type and dosage, and combination of NC with other admixtures to achieve the desired early-age properties for successful execution.

6. Conclusions and directions for future work

This paper presented a review of the current state-of-the-art on the use of NC in cement-based materials. NCs are often used as thixotropy modifiers and have been found to be effective in facilitating select casting applications compared to micro-sized, less processed clays. This has motivated a number of studies on the effect of NC on cement rheology (Section 2) and fresh microstructure (Section 3), which have shown they can enhance structural build-up and flocculation behavior, respectively. Presently, most studies have focused on structural build-up as characterized by static yield stress evolution. However, as a nanoparticle, NC have been shown to alter hydration behavior, and their role as seeding materials and how that impacts structural build-up should be better understood. Therefore continued work on the effect of NC on early hydration via oscillatory shear, laser spectroscopy, calorimetry, etc. and clear connections to flow behavior would be beneficial to separate their colloidal versus hydration effects on structural build-up, as well as underlying flocculation and coagulation behavior.

For tailoring rheology for casting applications, attapulgite NC has been investigated more than any other NC type. It is worth exploring other types of NC for potential advantages in performance, availability, and cost. In contrast, more NC types, i.e. kaolinite and metakaolin NC, have been investigated in studies that focus on the durability properties, i.e. chloride penetration, freeze-thaw and corrosion resistance (Section 4.4). There is an apparent mismatch between the NC types investigated between the early-age versus long-term properties. Therefore, in addition to exploring a more diverse group of NCs, there needs to be more coordination between the two areas of study. And along these lines, exploring the potential benefits or pitfalls of NC should be extended to other performance properties, e.g. alkali-silica reaction, concrete adhesion, surface smoothness, and fire resistance.

Although NCs have been found to be effective for more conventional formwork casting application (Section 5.1–5.3), further understanding and development are necessary to make them effective admixtures for extrusion-based 3D concrete printing, as the loading imposed on the material will be different and thixotropic demands will be higher due to the absence of formwork. As mentioned in Section 2.1.4, the stress conditions on the freshly deposited material are different in 3D concrete printing when compared to formwork casting, i.e. higher presence of internal stress at rest. Therefore this should be taken into consideration during rheological characterization of yield stress and elastic properties, which is currently a highly under-investigated area in cements. Additionally, early studies on the use of NC for 3D concrete printing have generally shown that although NC does offer advantages in extrudability and shape stability, there are some shortcomings, i.e. insufficient green strength development or excessive stiffness leading to brittle behavior (Section 5.4). This highlights that current processing techniques (i.e. adding in the dry, as received state or shear mixing in water) and NC alone are not sufficient to achieve desired printing properties. This motivates further study in two key areas: i) enhanced dispersion of NC and ii) NC-admixture interactions.

The presence of a threshold level for NC has been observed in fresh and hardened properties, as mentioned throughout this paper, which has been attributed to dispersion issues. Therefore improved dispersing techniques, e.g. chemical modification, mechanical treatment, functionalization, synthesis, or combination, would enhance their effectiveness, allow for higher loadings, and avoid adverse effects due to aggregation, such as increased shrinkage or decreased mechanical performance. Improved dispersion of NC for cements will go hand-in-hand with robust quantification of dispersion (ex-situ and in-situ), effective dosing during production, i.e. as a slurry or dispersed in solid form, as well as other practical considerations. Even with such advancements, it is inevitable that NC will be incorporated in mixes that are modified with a variety of admixtures, i.e. setting accelerators, superplasticizers, viscosity modifying agents, especially for applications like 3D concrete printing. Although NCs have been used and studied in concretes incorporating different admixtures, e.g. SCC and SFCC, detailed studies on NC-admixture interaction still remains a knowledge gap and can led to improved compatibility. For instance, chemical modification of NC can help control superplasticizer demand, which is generally increased in NC-modified mixes for a target flow.

CRediT authorship contribution statement

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Declaration of competing interest

The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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