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3D printing concrete containing thermal responsive gelatin: Towards cold environment applications

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\textbf{A R T I C L E  I N F O}

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\textbf{A B S T R A C T}

Construction with cementitious materials via 3D printing requires a highly thixotropic behavior, which is a challenge for construction industry. In this work a facile and low-cost gelatin-modified thermal responsive smart cement paste formulation was developed for extrusion-based 3D printing in cold environments. The paste’s temperature-dependent rheological properties were characterised, and the underlying mechanism was explored. At room temperature, the modified paste presents similar rheological properties as the reference cement paste. After resting for 10 min at 5°C, the modified cement paste has a yield stress of 1900 Pa which is 10 times that of the reference paste. Moreover, the mechanical properties of the modified paste are comparable to or higher than that of the reference paste at later age. Our approach may inspire a facile manipulation of paste rheology through temperature, which facilitates smartly controlled 3D concrete printings.

\section{1. Introduction}

Large scale additive manufacturing of cement-based materials has been hailed as a novel construction technology in the last few years which changes the traditional building practices via a computer-controlled positioning process to manufacture freeform constructions \cite{1,5}. The printing is done mainly by extruding fresh cement paste layer-by-layer through a fine nozzle which is controlled by a computer in compliance with a 3D model \cite{4,6}. This process imposes several contradictory requirements on the rheological properties of cement paste, such as pumpability, buildability and good interfacial strength between successive layers \cite{4,5}. While the pumpability benefits from a low viscosity and yield stress, buildability requires a high yield stress to ensure form stability \cite{7}. To suit such requirements, thixotropic materials are an ideal choice as they can be extruded smoothly, and after structuration are capable of holding the weight of the subsequent layers thereby ensuring shape stability \cite{8,9}. In order to improve the thixotropy of cement paste, viscosity modifiers such as nanoclay or welan gum are the usual choices \cite{10,11}. However, this strategy is passive, more importantly, the increased viscosity and yield stress make pumping more difficult. It would be more desirable to create a cement paste with stimulus responsiveness for 3D printing whose stiffening behaviour could be switched on demand. In the pumping process, the paste would be very flowable while after extrusion from the nozzle, it would set quickly to support the superposed layers.

As concrete is applied in various temperature conditions, cement paste that responds forthwith to thermal change has a great potential for the smart control of the rheological behaviour towards 3D printing concrete. However, traditional cement paste is not a material that has a quick thermal response. Functionalizing cement paste with thermal...
response materials can potentially address this challenge. Hydrogels, consisting of a polymer network in an aqueous matrix, form a material class for which thermal response variants are readily available [14–17]. Such behaviour can result from thermo-reversible covalent cross-links or physical cross-links based on temperature dependent non-covalent interactions such as hydrogen bonds, hydrophobic association or metal-ligand interactions [18]. Thanks to their stimulus responsiveness and wide variety of molecular design parameters, the development of printable hydrogels is an active research area [19,20], which may also facilitate the development of novel cement paste suitable for 3D printing. For example, when used in a cold environment, the hydrogel precursor (in the form of powder) can be first dissolved easily in hot water and then used for preparation of a highly flowable cement paste. Once the cement paste is printed in cold environment, the hydrogel starts to cross-link which will provide a sufficient yield stress to withstand the weight of the printed structure. Until now this approach remains barely reported in concrete printing field.

This study aims to present an innovative approach to thermally control the fresh state performance of cement paste towards 3D printing applications as shown in Fig. 1. Through controlling the working temperature, the fresh properties of the cementing operations can be adjusted. Gelatin is chosen as the target thermal-response hydrogel owing to its low cost [21,22], facile preparation [23], excellent thermal response behaviour [24,25] and proven performance in 3D printing for food and pharmaceutical applications [26,27]. The influence of the dosage of gelatin on the rheology of the cement pastes under different temperatures was investigated. The mechanism of the gelatin functionality in the cement paste was revealed by low-field $^1$H NMR. Our work targets to present a novel approach to engineer the thixotropy of cementitious materials for 3D printing in cold environments.

2. Experimental

2.1. Materials

Portland cement (CEM I 42.5 N) and gelatin powder (gelatin from porcine skin, type A) from Sigma were used in this work. The detailed oxide composition of the cement was measured by X-ray fluorescence (Table 1).

The gelatin powder was first dissolved in hot de-ionized water (80 °C) by magnetic stirring for 0.5 h after which the gelatin powder is completely dissolved. Three dosages (1%, 2% and 3%) of the gelatin powder were added in water and the as prepared solutions were denoted as G1, G2 and G3. Subsequently, the gelatin solutions are cooled down to 23 °C in a temperature-controlled oven. Then the gelatin solutions are mixed with cement at a water/cement (w/c) ratio of 0.4. The as prepared cement pastes are denoted as CP1, CP2 and CP3, respectively. For the reference cement paste, noted as Ref, only de-ionized water is used with a w/c ratio of 0.4. All the cement pastes are mixed by a hand-hold mixer with a speed of 1000 rpm at 23 °C for 2 min.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The chemical composition of the binders used in this study (wt.%).</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>CaO</td>
</tr>
<tr>
<td>wt.%</td>
<td>14.38</td>
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</tbody>
</table>

2.2. Testing methods

2.2.1. Rheological measurements of fresh cement pastes

2.2.1.1. Equipment and geometry. The rheology was studied by an Anton Paar MCR 501 rotational rheometer with a CC27-SS grooved coaxial cylinder geometry. The grooved bob and wall surface of the cup are specially designed for cementitious systems to prevent wall slip, thereby ensuring that bulk properties can be measured. The diameter of the bob is 27 mm with a gap distance of 1 mm to the cup. The gap between the bottom of the bob and that of the cup is set as 1 mm. The rheometer is equipped with a Peltier temperature control system which can change the temperature from –20 °C to 100 °C.

2.2.1.2. Small amplitude oscillatory shear (SAOS) test. For the SAOS tests, 15 ml of the gelatin solutions or cement paste (stored at 23 °C) was added into the cup. Then the bob was lowered to the designated position of 1 mm from the bottom of the cup. To determine the transition temperature, the temperature of the cup was set to decrease from 25 °C to 5 °C at 10 °C/min. To obtain the time evolution of the storage modulus, we performed SAOS time sweep measurements on fresh samples. The details of the method can be found elsewhere [34]. In a preliminary test, a strain sweep was conducted to determine the linear viscoelastic domain (LVED) wherein the storage modulus $G’$ is independent of the applied shear strain amplitude. In a similar manner, a frequency sweep was performed to determine the frequency dependency of the moduli. All samples are kept at 5 °C for 10 min in the rheometer before the frequency sweep and strain sweep test. Based on the sweeps, an angular frequency of 1 Hz and strain value of 0.0001 were chosen to measure the storage modulus evolution as a function of time and/or temperature.

2.2.1.3. Static yield stress. To obtain the static yield stress, stress growth measurements were performed by applying deformation at a constant shear rate of 0.1 s$^{-1}$. The shear stress was progressively developed to a maximum value and then decayed to an equilibrium value. The static yield stress is defined as the peak shear stress value [10,28]. Before loading the samples, the temperature of the rheometer was quenched to the desired temperature. As this method is destructive, new samples are prepared for each yield stress measurement.

2.2.1.4. Dynamic yield stress and plastic viscosity. The equilibrium flow curve at different temperatures was obtained by plotting the stress at each step versus the corresponding shear rate. Before loading the samples, the temperature of the rheometer was quenched to the desired
temperature. The cement pastes were sheared at rates of 600 s$^{-1}$, 500 s$^{-1}$, 400 s$^{-1}$, 300 s$^{-1}$, 200 s$^{-1}$ and 100 s$^{-1}$ for 60 s each and the shear stress at the end of each step was used for the fitting process. The Bingham model was used to fit the equilibrium flow curve to obtain the dynamic yield stress and plastic viscosity [29] as shown in Eq. (1):

$$\tau = \tau_y + \mu \dot{\gamma}$$  

(1)

where $\tau_y$ is the dynamic yield stress; $\mu$ is the plastic viscosity; $\dot{\gamma}$ is the shear rate.

2.2.1.5. Compressive strength test. Compression tests of the gelatin hydrogel and the thermal response cement paste were carried out with a universal testing machine (SHIMADZU, SHIMADZU Co., Ltd.) at a displacement rate of 1 mm/min with the maximum strain set at 70%. The gelatin and thermal response cement pastes were first poured in a cylindrical plastic mould with a diameter of 2 cm, and then stored in a 5°C fridge for 10 min. Then the samples are taken out from the moulds and a Vernier calliper is employed to measure the diameter and height of the samples. Dino recording system was used to record the loading process of the machine and deformation of the samples. The recorded movies are provided in S1 and S2. An average elastic modulus is calculated as the slope of the line that connects the origin and the first maximum, which corresponds to the largest elastic deformation.

2.2.2. Setting time For the setting time test, the water or gelatin solution and cement were first added into a cement paste mixer and mixed at 300 rpm for 1 min. The homogeneously mixed cement paste was then decanted into the mould for the Vicat test. The moulds were cured in a temperature controlled oven at 5°C and 20°C respectively. The setting times of the cement pastes were evaluated by using the Vicat apparatus based on European Standard EN 196-3 [30].

2.2.3. Low-field NMR Low-field NMR is employed to reveal the water transport process during the gelation of the thermal response cement paste. The experiments were performed with a home built NMR setup which has been previously reported in Refs. [31,32] with a static magnetic field of 0.7 T, resulting in a resonance frequency value of 31.57 MHz and a gradient of 400 mT/m, with a theoretical spatial resolution of 0.8 mm. Spin–spin relaxation time ($T_2$) values were obtained by a conventional CPMG pulse sequence, using similar settings as the Hahn spin echo sequence, with an echo time of 150 μs, 512 echoes, recording window of 100 μs, repetition time of 2.5 s, pulse length of 9 μs and 16 averages at different sample positions. A cylindrical Teflon tube with an internal diameter of 10 mm is used to load the cement paste and the height of the cement paste loaded is 8 cm. A water bath cooling system was used to control the temperature of the test and the temperature is set at 5°C during the measurements.

2.2.4. SEM Freeze dried gelatin and cement paste containing gelatin were submitted to Scanning Electron Microscopy (JEOL JSM-6390LV) for microstructure observations. The G3 and CP3 cement pastes were stored at 5°C for 10 min and then frozen in liquid nitrogen, fractured and gold coated before analysis by SEM in secondary electron mode at 5 kV.

2.2.5. Mechanical properties of the hardened cement pastes The influence of the gelatin on the mechanical properties of cement pastes at different temperatures is investigated. The flexural and compressive strengths of the hardened cement pastes at ages of 1, 7 and 28 days were determined according to EN 196-1 [33], under curing temperatures of 5°C or 20°C. For the printing samples of CP3, the flexural and compressive strengths of the hardened cement pastes with ages of 1, 7 and 28 days were also determined according to EN 196-1 [33]. The cement pastes were printed by an electric caulking gun with a rectangular nozzle on its top and the printed layer is 50 mm wide and 10 mm high. The samples were printed in a cold-water environment (5°C) and the interlayer time for the sample printing was 10 min. The three-layer printed samples were cut with a length of 160 mm for the flexural strength test and 50×50 mm$^2$ shape for the compressive strength test. In both cases the loading direction is perpendicular to the printed layers.

3. Results and discussions

3.1. Rheological characterization of the fresh cement pastes

3.1.1. SAOS test results of the cement pastes The evolution of the storage modulus with temperature for the gelatin solutions is shown in Fig. 2(a). Upon cooling, the material undergoes a transition from a viscous solution (G′ ≈ 0 Pa) to an elastic gel. This gelation is caused by a transition of the gelatin molecules from a random coil to the helix state, whereby triple helices form the cross-links of the gelatin network [25]. The gelation temperature increases from 11.2°C to 19.8°C when the dosage of gelatin increases from 1% to 3%. This is in line with previous researches, whereby higher dosages of gelatin introduce a larger number of bonds from the protein-protein and protein–solvent interactions which make gelation easier [34,35]. A similar trend can be found in the storage modulus evolution with time at 5°C shown in Fig. 2(b). The storage modulus of G3 increases faster and reaches a higher plateau value than that of the other two samples which suggests a quicker and more complete gelation process.

The results of the strain sweep measurement for the G3 gel and cement pastes cured at 23°C or 5°C are shown in Fig. 2(c). Up to a critical strain, the storage modulus (G′) remains independent of the applied strain. In this strain region, only reversible deformations occur, also known as the linear viscoelastic region (LVR). The G3 presents a wider LVR (up to 10$^{-1}$) than the cement pastes. When increasing the applied strain beyond the LVR, the G′ of G3 increases which depicts a typical strain-stiffening behaviour as shown in Fig. S3, observed before for gelatin gels [36]. Mentioned causes for this behaviour include the finite polymer length, the fractal structure of the polymer strand and the combined presence of stiff rods and flexible coils [37]. Cement paste has a completely different behaviour, showing the typical strain softening exhibited by colloidal suspensions. The addition of gelatin has resulted in a decrease of the LVR of the cement paste at 23°C, when it is in the dissolved state. However, at 5°C, CP3 presents firstly the strain softening originating from the particle network, followed by an obvious decrease of the strain softening when the applied strain is larger than 2 × 10$^{-3}$.

The experimental results for the storage modulus evolution of the cement pastes are shown in Fig. 2(d). At 5°C, the G′ of CP3 is similar to that of Ref. These findings suggest that CP3 at 5°C formed gelatin-cement networks, demonstrating elastic behaviour. The modulus is expected to be determined by two counteracting effects. First, the reduced water availability for the cement particles and gelatin molecules due to their co-presence, which would increase the modulus of the gel network. Meanwhile, cement paste forms a much stronger particle-network than the softer polymer-based network of the gelatin chains. Hence, incorporation of gelatin chains may lower the overall network modulus by replacing particle-particle contacts with particle-polymer contacts.

3.1.2. Static yield stress and young’s modulus of the cement pastes The static yield stress is measured by a stress growth measurement as shown in Fig. 3(a). At 5°C, the yield stress of the cement pastes increases with the addition of gelatin. The cement paste with 3% gelatin (CP3) presents a yield stress of around 1900 Pa which is 10 times the yield stress of the reference cement paste. The static yield stress of the cement pastes at different temperatures is shown in Fig. 3(b). The yield stress of all CP samples increases with decreasing resting temperatures. At lower
temperatures, the driving force for gelatin cross-linking is higher. The static yield stress evolution with time at 5 °C is shown in Fig. 3(c). The Ref cement paste shows a slight increase of the yield stress with time from 98.5 to 140.3 Pa. This is because at the early stage of cement hydration, the reaction speed is very slow and the reaction has little influence on the rigidity of the cement paste. This is a drawback for 3D printing when a rapid yield stress growth is needed to hold the weight of the successive layers. For the gelatin containing cement paste, the growth of the yield stress is substantial. A complete steady state is not yet reached after 10 min, but the yield stress of CP3 has increased by a factor of 13 in this timespan.

The compression stress-strain curves of the G3 and CP3 cement pastes after curing at 5 °C for 10 min are shown in Fig. 4. For the Ref cement paste, it is still very flowable after curing at 5 °C for 10 min.
therefore cannot undergo the compressive test. The relationship between stress and strain of G3 is nonlinear and shows strain-stiffening. G3 also presents an excellent deformability since it deforms at around 58% strain with a stress of $9 \times 10^3$ Pa. Once the load is applied, the polymeric chains of the gelatin are reoriented with changed relative positions, while the free water begins to drain and escapes from the hydrogel. It is possible to achieve a significant deformation from the application of a relatively small load. It should be noted that when the load exceeds a critical value, the material edge starts to fracture, which is a failure feature that is related to the geometry of the test. When mixed with cement, the material deformability is weakened while the carrying capacity is largely increased. At 10% strain, the stress is $1.3 \times 10^5$ Pa. Meanwhile, the compressive curve exhibits a linear response over a much wider range of strain values. When comparing the Young’s modulus, it can be concluded that the one from CP3 is 100 times that from G3.

3.1.3. Dynamic yield stress and plastic viscosity of the cement pastes

The shear stress versus shear rate and corresponding Bingham model fitting is shown in Fig. 5(a). The equilibrium flow curves of the samples are linear and could be fitted well with the Bingham model (Eq. (1)). The dynamic yield stress and plastic viscosity obtained from the flow curve model fitting are shown in Fig. 5(b) and (c). In line with its influence on the static yield stress, the addition of gelatin results in an obvious increase of the dynamic yield stress and plastic viscosity of the cement pastes. At 5 °C, the dynamic yield stress and plastic viscosity of CP3 is around 10 and 4 times respectively that of the reference cement paste (Ref). It should be noted that a high dynamic yield stress and viscosity are not helpful for printing of the cement paste as it will require more power for pumping. Therefore, the ideal application situation for this temperature responsible cement paste is mixing and transporting at room temperature and then printing into an environment at lower temperature. As compared to the reference paste, which exhibits an insignificant dependence of the rheological parameters on the temperature, the dynamic yield stress and plastic viscosity of CP3 increase 11 and 3.5 times, respectively, when lowering the temperature from 23 °C to 5 °C.

3.2. Microstructure and loading capacity of the thermal responsive cement paste

The microstructures of the G3 and CP3 are shown in Fig. 6 (a)-(d). For G3, loose fibrous network structures with 20–50 μm pores can be found as shown in Fig. 6 (a) and (b). The surface of the network is smooth and a high content of free water can be locked in the pores. Because of the microstructure, gelatin will undergo a large deformation when imposing a large load, resulting in easy fracture as shown in Figs. 4 (a) and Fig. 6 (e). When the gelatin solution is mixed with cement and stored at 5 °C, the gelation happens with cement particles distributed in the network of pores, which is shown in Fig. 6 (c) and (d). In Fig. 6 (c), a clear gelatin-based crosslinked structure with cement particles distributed in the network can be found. While in Fig. 6 (d), aggregating cement particles bonded by gelatin are presented.

The above structures provide further explanation for the enhanced mechanical performance of the thermal response cement paste at low temperature. Cement particles can not only be absorbed to the skeleton...
of the network but can also aggregate and fill the network pores which reduced the spaces between the interlayers and compacted the network. When the low temperature cured CP3 is subjected to compression or oscillatory shear, the friction and resistance to viscous flow between the sliding layers increased, resulting in a larger compressive strength and viscoelastic moduli which has been proven by the rheology and mechanical tests above.

3.3. Water transport processes in the cement pastes at early age

The $T_2$ relaxation time of the reference cement paste and CP3 at 5 °C as a spectrum were obtained as shown in Fig. 7 (a) and (b), where different peaks in $T_2$ can be attributed to water in different states. Both samples present three peaks in the spectrum. In hydrated ordinary Portland cement, P1, P2 and P3 are often assigned to C-S-H gel water, capillary water and water in a larger space [37,38]. The increased $T_2$ from P1 to P3 is mainly due to the time it takes for activated water molecules to be relaxed by the ferromagnetic solid surface nearby, which increases at a more open space [39,40]. Under the same principle, our recent work assigns P1, P2 and P3 to the water at the vicinity (several nm) of the cement surface, water in a confined space (less than one μm), and water in large voids, for paste that has not yet solidified [38]. This assignment is considered here as the pastes were also not yet solidified. Note that a pure gelatin solution (G3) has one dominant $T_2$ peak near 1 s throughout the measurement time (shown in S4).

The peak area percentage evolution of each peak during the test is shown in Fig. (c) and (d). At 5 °C, CP3 presents a larger P3 peak area percentage than the reference sample, suggesting that a slightly larger portion of water molecules are relatively distanced from cement particles. This could be attributed to the fact that the gelatin molecules separate the cement particle agglomerations, such that the confined space between the cement particles is reduced. The increased area percentage of the P3 peak from 6 min to 18 min in CP3 suggests that more free water was absorbed by the hydrogel during the gelation process. The absorbed water is beneficial for the continuous hydration of the paste particularly in a dry environment, which is often experienced for 3D printing without a formwork to restrict surface drying [41,42].

3.4. Setting time and mechanical properties of the hardened cement pastes

Fig. 8 Shows the influence of gelatin on the initial and final setting time of the cement paste at 5 and 23 °C, respectively. Both the initial setting time and the final setting time were extended at 5 °C as compared to 23 °C. For Ref, the initial setting time increases to 250 min at 5 °C.
This is because the low temperature retards the cement hydration and therefore the cement paste requires much longer time to set. The addition of gelatin slightly increases the initial and final setting time of the cement pastes. However, the retardation effect due to gelation is less pronounced than the influence of the temperature.

The influence of the gelatin on the evolution of the mechanical properties of the cement pastes at 23°C and 5°C is shown in Fig. 9. Both the compressive and flexural strength show an obvious decrease when the curing temperature decreases from 23 to 5°C which is in line with its influence on the setting time. It is discovered that the incorporation of gelatin has little influence on both the compressive and flexural strength at 23°C on 7d and 28d while an increase can be found at 5°C on 7d and 28d. This can be attributed to the later hydration of dicalcium silicates (C₂S) of the cement. The slow heat release process is beneficial to limit the generation of micro-cracks for the application of 3D printed concrete as the absence of formwork results in a fast pore water evaporation.

In order to provide a low temperature environment for printing, the thermal response sample is printed in cold water with a temperature of 5°C as shown in Fig. 10(a). The comparison of the compressive and flexural strength between the casting CP3 and the printing CP3 is shown.
in Fig. 10 (c) and (d). For the compressive strength, the printing hardened sample is slightly weaker than the casting one. This is in line with other research [43,44]. For the flexural strength, the printing sample presents a little higher performance than the casting one.

4. Conclusions

A simple and low cost thermal responsive cement paste towards 3D printing for cold regions is formulated based on gelatin. At room
similar to that of the reference cement paste. When extruded at low temperature, the gelatin mixed cement paste presents a good flowability and slow release of water from the cross-linked gelatin which suppresses the formation of micro-cracks.

The printed samples present a similar mechanical performance compared to casted samples, which demonstrates the interlayer bonding.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cemconcomp.2023.105029.

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