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# Dynamic and static yield stress determination of cementitious paste with admixtures

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**Abstract.** The 3D printing of cementitious material requires an understanding of the printing material's rheological properties, especially yield stress and viscosity. The ability to adjust and control these properties in the 3-D printing process represents a breakthrough for the construction sector. The aim of this paper is to experimentally determine the dynamic yield stress and static yield stress of cementitious materials with admixtures. Unlike conventional rheometer geometries, the National Institute of Standard and Technology (NIST) spindle geometry is used in this work for the measurement of both yield stresses. While dynamic yield stress was measured by increasing and decreasing the rotational velocity, the static yield stress was characterized by two methods: the torque increase method and the constant rotational speed method. For both yield stresses, a total of 16 mixtures were studied in a factorial experimental design of the chemical admixtures. The impact of each admixture has been highlighted. The structural build up was assessed through the structuration rates. The temperature effect on the early age properties was studied for the most promising formulations.

**Keywords:** Cement paste, admixtures, dynamic yield stress, static yield stress, structural build up, temperature.

## 1. Introduction

In recent years, many industrial sectors have innovated in manufacturing methodology to take advantage of new technology. However, the construction field continues to be limited to conventional formwork methods for precast concrete and cement-based products. Developed in the 2000s, 3-D printing and additive manufacturing present a paradigm shift in production methodology. With computer assistance, 3-D printing can overcome difficulties of conventional formwork-based techniques, such as precise deposition, material solidification process and material volume quantification [1]. Furthermore, 3D-printing has the potential to reduce the manufacturing time by replacing both the casting and molding production steps [2]. The printing process consists of material extrusion and layer by layer deposition. Utilization of this technique necessitates a deeper understand of how to control the material flow. Determining the mechanical conditions for flow in cementitious materials

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is complicated by the use of admixtures which modify the rheological and mechanical properties [2]. The flow conditions vary with formulation parameters such as the type of admixtures, the time of addition [3], and the physical form of the mixture [4]. For consistent extrusion rates at reasonable pressures, the mixture must exhibit a certain degree of fluidity. In addition, the static integrity of a material layer must exceed a certain level to enable the deposited layer support the subsequent layers [2]. While the fluidity of the material may depend much on its viscosity, the stability of the printed layer is a product of the yield stress. At the microscopic scale, the yield stress is a measurement of the force required to overcome the interparticle attractions within the suspensions of the cementitious material [5]. Due to thixotropic nature of cementitious pastes, two different yield stresses are considered when describing the material's rheological properties: the dynamic yield stress and the static yield stress. In this work, the yield stress measurements were carried out using a rotational rheometer equipped with a spindle geometry [6]. Calibration methods [6] were followed to determine both dynamic and static yield stress of the mixtures obtained from combinations of different admixtures. The structural build up was assessed using linear equations developed in others works [6, 7]. Finally, the effect of temperature on the dynamic yield stress was explored.

## 2. Material and methods

The experiments in this work were conducted with 8% by weight silica fume added to Portland cement in a mixture known as GUb-SF with a specific gravity of 2.8. Sixteen different formulations were designed from a combination of admixtures: superplasticizer (SP), accelerator (A), C-S-H seeds (X), nano-clay (C) and viscosity modifying agent (VMA). Design details of the formulations are given in Table 3 of [2]. Based on the preliminary studies conducted with the paste and per the recommendation of the concrete producers, a water-cement ratio of 0.345 was chosen with tap water. As most of the admixtures take the form of aqueous solutions or suspensions, the addition of water (effective water quantity) was adjusted to account for this and maintain this constant ratio. The admixtures modify the rheological properties of the fresh cementitious paste to the requirements of the 3-D printing process as studied by several researchers in the past [3, 4]. Microstructural inhomogeneities are known to cause variations in rheological properties [8]. For this reason, it is important to select a suitable mixing procedure to maximize homogeneity. The mixing procedure certified by NIST was followed in this study [6]. First, the appropriate amount of water and admixtures was poured into the mixer at room temperature of 23 ºC. The cement was added within 60 seconds. The mixture is blended with a high-speed mixer at 10 000 rpm for 30 seconds. Following this, a rest time of 150 seconds is given to the paste before a final mixing step for 30 seconds at the same speed. The measurement of the dynamic yield stress was initiated 5 minutes after the mixing procedure. A total of 35 measurements were recorded by increasing and decreasing the angular velocity in the range of 0.1 rpm to 100 rpm in a hysteresis loop. The full test was conducted in 17 minutes with a measurement every 30 second or until the torque stabilized. From the collected data of the 16 mixtures, the shear stresses were computed as functions of the shear strain for each increasing and decreasing angular velocity. The conversion of angular velocity and torque to shear stress and shear strain, respectively, was possible from NIST calibrated models with the calibration factors $K_\tau$ and $K_\mu$, 11939 Pa/Nm and 2.190, respectively.

## 3. Results

### *3.1 Dynamic yield stress*

The dynamic yield stress was calculated as the intercept of the linear regression of the stress-strain curve of decreasing angular velocity for each of the 16 formulations. The design and composition of the 16 mixtures is described in Table 3 of [2]. The results of these calculations are shown in Fig. 1, labeled by the acronyms of the admixtures present in the formulation. The lowest dynamic yield stress was observed to be 5.35 Pa in mix 5, which incorporated the ready-mix accelerator. The highest value was in mix 12 at 28.60 Pa.

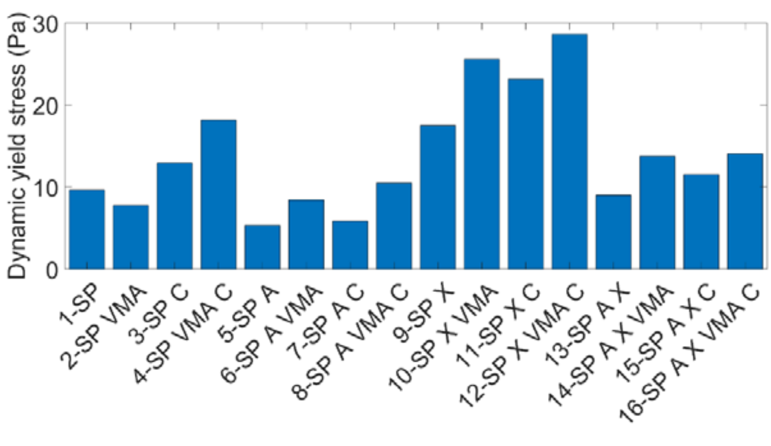


Figure 1: The dynamic yield stress of each of the formulations compared in this study

#### *3.1.2 Effect of temperature*

The effect of the temperature on the dynamic yield stress was studied on a few arbitrarily selected mixtures as detailed in Fig. 2. The measurements were carried out at the temperatures of 5°C, 15°C, 23°C, 30°C and 40°C. Below the temperature of 30 ºC, a fluctuation of the dynamic yield stress was observed for mix 7 (SP A C) and mix 16 (SP A X VMA C). For mix 13 (SP A X) and mix 14 (SP A X VMA), the yield stress increased monotonically in the temperature range. The highest value, approximately 30 Pa, was recorded at 40°C for mix 16 (Fig. 2). In contrast, the plastic viscosity of the pastes decreased in the range of 5 °C to 40 °C

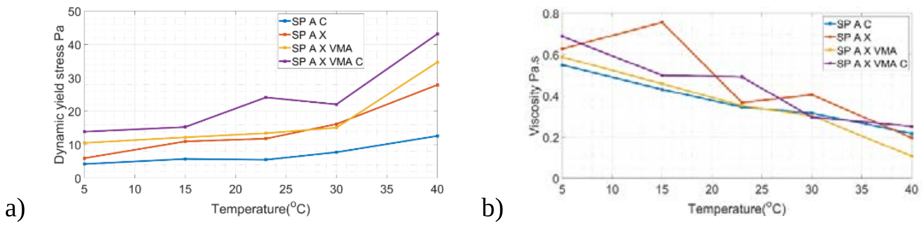


Figure 2: The effect of temperature on the a) dynamic yield stress and b) viscosity on selected mixtures

### *3.2 Static yield stress*

The results of the static yield stress tests of the mixtures are presented below. Measurements were completed at 13, 31, 51 and 71 minutes. After each test, a rest time was allowed for the mixture to undergo structural build up for the subsequent measurement. The calibration factors used in the calculation are 11916.213 Pa/Nm and 2.711 for $K_\tau$ and $K_\mu$, respectively.

#### *3.2.1 Torque increase method*

Data was collected every 30 seconds by increasing the torque from 0 to 8 Nm, or until the angular velocity reach 150 rpm, for a total of 60 measurements recorded over the range of the torque. Fig. 3 shows the evolution of static yield stress over time for the different mixtures. As expected, most mixtures exhibit a static yield stress increase with time. For example, the static yield stress of mix 1 (SP) at the time of 53 min experienced an average increase of about 27 Pa. However, a reduction of approximately 30 Pa was observed for some mixtures, such as mix 5 (SP A) and mix 7 (SP A C).

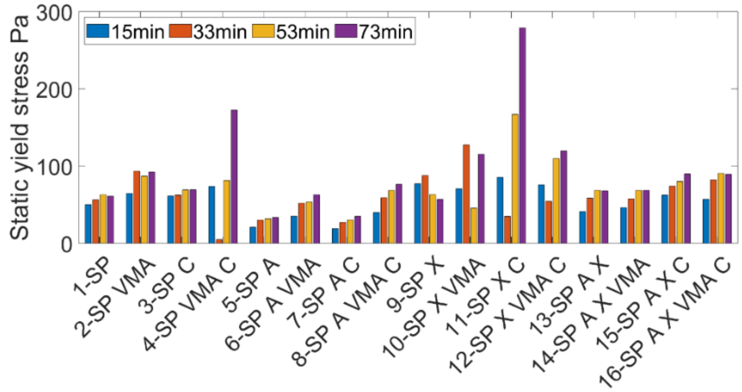


Figure 3: The static yield stress of mixtures at different times by the torque increase method

#### *3.2.2 Constant speed method*

Fig. 4 shows the time dependence of the static yield stress of 16 different mixtures by the constant speed measurement method. The static yield stress of most of the mixtures did not increase with time, except mix 4 (SP VMA C) and mix 9 (SP X) to mix 12 (SP X VMA C) where a significant increase was observed. For these five mixtures, there is an average increase of approximately 160 Pa between the 33$^{rd}$ and 53$^{rd}$ minute and more than 300 Pa between the 33$^{rd}$ and 73$^{rd}$ minute. The structuration rates for these five mixtures are given in Table 1

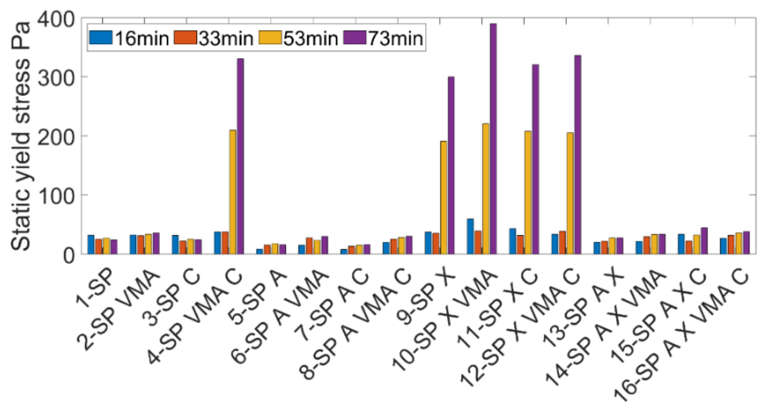


Figure 4: The static yield stress of 16 mixtures at different times by the constant speed method

Table 1: Structuration rate for select mixes as measured by the constant speed method (Pa/min)

| | Mix 4 | Mix 9 | Mix 10 | Mix 11 | Mix 12 |
|---|---|---|---|---|---|
| 16min-33min | 0.0057 | -0.1257 | -1.2051 | -0.6752 | 0.2980 |
| 33min-53min | 8.6069 | 7.7885 | 8.9300 | 8.7885 | 8.3365 |
| 53min-73min | 6.0302 | 5.4020 | 8.5845 | 5.6645 | 6.5110 |

## 4. Discussion

The ability to modify and fine-tune the rheological properties of a material is essential for 3D printing. The 16 formulations studied in this work lay the groundwork for the experimentation required to create a full rheological adjustment function for use in 3D printing applications. As was studied here, this function must consider the admixture proportions, temperature effects, and time dependence.

Fig. 1 shows the dynamic yield stress variation with the chemical admixtures. Mix 1 (SP) is taken as reference since it contains only the superplasticizer (SP). C-S-H seeds (X) and nano-clay (C) are responsible for formulations with the highest values of dynamic yield stress such as mix 12 (SP X VMA C). The C-S-H seeds alone contribute to the strengthening of the cement paste which can be seen in mix 9 (SP X) of Fig.4. A decrease in the dynamic yield stress was observed in some mixtures due to the accelerator (A) and the viscosity modifying agent (VMA). The accelerator used in this study was designed for ready-mix concrete which combines an accelerating effect with a lengthened induction period to allow for transport. For this reason, the accelerator has the expected effect of prolonging the fluidity of the paste. It can still be useful for 3D printing, to prepare batches in advance. From this it is interpreted that the measurements were conducted before the hydration peak was reached for the formulations with the accelerator.

Temperature was observed to have a significant impact on the dynamic yield stress. For the arbitrarily selected mixtures, the temperature was shown to positively increase the dynamic yield stress in the range of 5 to 40°C (Fig 2). While the dynamic yield stress increases up to 40°C, the viscosity was observed to reduce significantly for all the selected mixtures. The fact that both dynamic yield stress and viscosity increase and decrease, respectively, with temperature is surprising. However, it has been reported in literature that the temperature is responsible for two opposing effects in the yield stress of cementitious material [9, 10]. First, the yield stress decreases with temperature due to accelerated particles mobility and aggregation breakdown [9]. Second, elevated temperature accelerates binder hydration which increases the yield stress [9, 10]. Temperature acceleration of hydration reactions is well known in the literature for cement and other binders [10-12]. This duality explains the seemingly contradicting expectations of the impact of temperature. The viscosity decreases due to deagglomeration, while the yield stress increases due to accelerated hydration. This suggests temperature variation could be incorporated in 3D printing process design for reducing slump during deposition and rheological properties adjustment. However, further study is needed to more thoroughly understand the mechanisms behind the dynamic yield stress and viscosity trends with temperature. In addition, it will be important to document the influence of temperature on the structuration rate as the structure of printed layers is known to be affected by hydrostatic pressure over time [4, 13, 14]. The time between two consecutive printed layers is variable with the 3D printing technique and, as identified in this example, is significant to the material stability. Future work must elucidate the temperature conditions to optimize the material properties for suitable print stability.

With regards to the static yield stress, a large gap was observed between the two methods of measurement as detailed in Fig. 3 and Fig. 4. In general, the torque increase method, Fig. 3, measured only a modest impact of the admixtures on the static yield stress. The small increase with time can be attributed to yield stress development during the rest time rather than the chemical effect of the admixtures. The exceptions to this trend in time are the mix 5 and mix 7 which are a consequence of the accelerator in those formulations by the phenomenon described earlier. However, when the accelerator is used in combination with the other admixtures, the same general trend is followed, as in mix 8 (SP A VMA C) and mixes 13 to 16. In contrast to most of the measurements, a considerable increase of static yield stress was recorded for mix 4 (SP VMA C) and mix 11 (SP X C) between the 53$^{rd}$ and 73$^{rd}$ minutes of rest time. Notably, for the same mixtures there is a reduction in yield stress between the 33 and 16 minute measurements. This is most likely due to a history effect from the previous measurement. For most of the mixtures, the viscosity was low enough for the applied torque to cause no observable shift in angular velocity. However, for these mixes, which were also observed to have the highest dynamic yields stress, and similar formulations additional precautions must be taken regarding the choice of the torque amplitude in order to avoid paste history effects and allow for comparisons to pastes of different viscosities at short rest times.

The second method of measurement tested, commonly known as constant rotational speed method, yielded interesting results as detailed in Fig. 4. However, as mentioned earlier, data collection was not possible at the age of 15 minutes due to a structural breakdown during the introduction of the paste into the rheometer. This implies that 15 minutes was not enough time for the paste to structurally build up before measuring. While the age and rest time played a role in the rise of the static yield stress, the chemical admixtures induced a significant increase in static yield stress for five mixtures (mix 4 and mixes 9 to 12) as shown in Fig. 4. A consistent difference between these five mixtures and others is the lack of accelerator which, decreases the yield stress. The ready-mix accelerator was designed to accelerate after a certain time to consider the transportation time. Comparisons between mix

4 and mixes 2 and 3, which have nanoclay (C) and viscosity modifying agent (VMA) alone, reveal that the observed trend is due to an interaction between the nanoclay and the viscosity modifying agent and not either of the admixtures alone. In contrast, mix 9, which contains only the C-S-H seeds (X), shows a similar increase in static yield stress to mixes 10 to 12 which include C-S-H seeds in combination with nanoclay and VMA. Therefore, combining these three chemical admixtures can help boost considerably the yield stress, particularly the C-S-H seeds and the VMA yielded the highest value of yield stress at 390 Pa in mix 10. This high value demonstrates capability of chemical admixtures to increase, in a short time, the structural build up which is defined by the structuration rate. As shown in Table 1, mix 10 has the highest structuration rate that is approximately constant about 8.75 Pa/min on average. The flocculation due to the nanoclay (C) and the C-S-H bridge formation are primarily responsible for the strong structural build up in these mixtures, as described in [15]. As explained above, the negative values of some of the structuration rate calculations can be explained by the influence of the rest time.

Comparing the two methods, the constant rotational speed method is best fit for these cement paste mixtures because of its low rotational speed. The paste is less disturbed by the measurement which enables quick structural recovery for the next measurement. Due to the thixotropic nature of cementitious materials, a measurement method which provides less disturbance to the paste is highly recommended by numerous authors [2, 13, 16]. However, this measurement method is not suitable for a more fluid paste. As the fluidity of these 16 mixtures varies with the chemical admixtures, other measurement methods need to be explored to enable broader research capability.

In the context of 3D printing, the same mixture must provide both strong static and dynamic yield stress. The effect of admixtures at a given age and temperature must fulfill this condition. For instance, as shown in Fig. 1, mix 12 at room temperature has the highest dynamic yield stress and the corresponding static yield stress (Fig. 3 and 4) at the same temperature are among the highest values. However, the time of the measurements is different. While dynamic yield stress is a measurement of the resistance to flow for a paste in flow, the static yield stress depends on the structural build up with time of the paste at rest as measured by structuration rates [7]. From these identified mixtures, the measurements of the static yield stress enable the study of the effect of admixtures. Further formulation refinement is required to create a suitable region of overlap for the regions of high dynamic and high static yield stress to optimize a cement mixture for 3D printing.

## 5. Conclusion

The dynamic and static yield stresses have been explored to determine the effect of admixtures in cementitious materials. Calibration factors from a geometry system known as spindle geometry, suggested by NIST, were used with linear and nonlinear fitting to calculate both yield stresses. The dynamic and static yield stresses values vary with the chemical admixtures. A large increase was recorded over time for static yield stress measured by the constant rotational speed method for mixes without the selected accelerator. This accelerator will become more interesting in studies on the build-up rate and of longer duration. To calculate the structural breakdown, the constant rotational speed measurement method was the most suitable for this cement paste. An increase of dynamic yield stress and decrease of plastic viscosity was observed above a certain temperature showing the possibility to control pumpability and printability with temperature. These results show early age property methods are a promising method to formulate and test materials for 3D printing, which require a high capacity for rheological properties control. Further investigation considering temperature, structuration rate and other measurement methods such as small amplitude oscillatory shear (SAOS) method is needed.

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