Evaluation of 3D printability of cementitious materials according to thixotropy behavior

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Abstract. This study is a basic research for evaluating the buildability of cementitious materials for three-dimensional (3D) printing. In the cement paste step, the thixotropy behavior according to the resting time, which represents the time interval between each layer, was analyzed. In addition, the relationship between the thixotropy behavior and 3D concrete printing buildability was derived by proposing a measurement method that simulates the 3D concrete printing build-up process. The analysis of the tendency of the thixotropy behavior according to the resting time revealed that the area of the hysteresis loop ($A_{hyst}$) showed a tendency to increase and then converge as the resting time increased, which means hysteresis loop approach critical resting time for sufficient buildability. In the thixotropy behavior analysis that simulates the 3D concrete printing build-up process, the buildup ratio, which is the recovery rate of the shear stress, showed a tendency to increase and then converge as the resting time increased, which are similar results like hysteresis loop. It was concluded that $A_{hyst}$ and the buildup ratio can be used as parameters for determining the resting time, and they have close relationships with 3D concrete printing buildability.

Keywords: 3D printing; buildability; thixotropy; resting time; cementitious material; rheology

1. Introduction

With the advent of the Fourth Industrial Revolution, the construction industry has made various attempts to apply three-dimensional (3D) printing to structural design and construction. Various industrial areas have focused on the research and development of 3D printing because it can increase freedom in design, shorten the production period, and reduce labor compared to existing processes. For the construction industry, basic research on 3D printing of concrete began overseas in 1997 with the method of additive manufacturing by extruding cementitious materials (Atrey et al. 2012, Cesaretti et al. 2014, Lloret et al. 2015, Zhang et al. 2013, Perrot et al. 2016). Some studies related to 3D printing have also been conducted since research on the development of 3D printing equipment and design technology for buildings was conducted. In addition, many efforts have been made for the commercialization of 3D concrete printing, such as conducting research on the development of 3D printing equipment and materials for small buildings and atypical members (Lee et al. 2017, Lim et al. 2011, Oh et al. 2014). Recent studies have focused on the optimal mixture of cementitious materials for 3D printing (Le et al. 2012a, Buswell et al. 2018, Marchon et al. 2018), development of a robot arm to additive manufacture atypical structures (Asprone et al. 2018, Reiter et al. 2018, Schwartz et al. 2018, Schutter et al. 2018), and constructing a 3D printing process that integrates the design, mixing, and extrusion processes (Chen et al. 2017, Hojati et al. 2018, Lowke et al. 2018, Roussel et al. 2018). Some advances have reached the commercialization stage.

There are three essential elements to 3D printing for concrete: design, equipment, and materials. For design and equipment, much basic data are already available from existing 3D printing industries. For materials, however, further consideration is required. Conventional 3D printing uses a single material such as filaments, but concrete is a composite material that mixes cement and aggregate. Therefore, various effects that depend on the properties of cementitious materials need to be considered, such as the properties of heterogeneous particles, curing properties over time, and different rheological properties depending on the mixing proportion (Ferraris et al. 2001, Goo et al. 2006). Moreover, performance evaluation methods need to be developed to secure the safety of 3D printed concrete structures. In particular, the material properties need to be evaluated before hardening (i.e., initial flow characteristics) because such structures are constructed through additive manufacturing without formwork, unlike conventional construction (Choi et al. 2014, Hwang et al. 2007, Koehler et al. 2005). The concept of rheology has been used to quantitatively and numerically evaluate the initial flow characteristics of materials, including cementitious materials. Rheology has been used to develop standard reference materials for cement paste (Lee et al. 2018a), establish guidelines based on an analysis of flow characteristics (Lee et al. 2018b), determine rheological properties according to concrete components (Benyamina et al. 2019), and devise evaluation methods for concrete...
Some studies have focused on the relationship between thixotropy and buildability of concrete. For this, the first step is to understand the thixotropic behavior of cementitious materials, such as shear stress, shear rate, flocculation and de-flocculation according to resting time. The next step was to derive the relationship between the hysteresis loop and the thixotropy model. In addition, a new measurement method for thixotropy was developed that simulates the additive manufacturing process of 3D printing for concrete. The developed thixotropy measurement method was correlated with hysteresis loop through quantitative analysis. Here, the resting time was used as a key factor in analyzing these relationships. Through these relationships, it is judged that thixotropy behavior can be used as one of the indicators to evaluate buildability for 3D concrete.

2. Thixotropy model and experimental setup

2.1 Thixotropy model

A thixotropy model for concrete was developed to evaluate the buildability of cementitious materials for 3D printing. Based on the general viscosity law of $\tau = \eta \dot{\gamma}$, the state of flocculation ($\lambda$), which indicates the degree of flocculation according to the shear stress and shear rate, can be expressed as (Cheng et al. 1965)

$$\tau = \eta(\lambda, \dot{\gamma}) \dot{\gamma},$$

where $\tau$ is the shear stress, $\dot{\gamma}$ is the shear rate, $\lambda$ is the state of flocculation, and $\eta$ is the viscosity. The change rate of the state of flocculation is equal to the difference between the flocculation rate of the material itself and the non-flocculation rate of the material due to its flow. This indicates that the change rate is proportional to the shear rate. Eq. (1) can be used to consider the flocculation inside the material to derive the following thixotropy model of concrete (Coussot et al. 2002)

$$\tau = (1 + \lambda)\tau_0 + \mu \dot{\gamma}^n,$$

$$\frac{\partial \lambda}{\partial t} = \frac{1}{\tau_0 m} - \alpha \lambda \dot{\gamma},$$

where $\mu$ is the plastic viscosity, $T$, $\alpha$ and $m$ are thixotropy parameters. By applying the Bingham model, which can linearly represent the flow of concrete, and assuming simplified thixotropy behavior, Eqs. (2) and (3) can be expressed as (Roussel et al. 2006)

$$\tau_c(t) = (1 + \lambda)\tau_{c0} = \tau_{c0} + \frac{\tau_{c0} \dot{\gamma}}{\tau} = \tau_{c0} + A_{thix} t$$

$$A_{thix} = \frac{\tau_0}{\tau},$$

where $\tau_c$ is the critical shear stress of the section where the shear strain $\gamma$ increases and converges, $\tau_{c0}$ is the critical shear stress when the resting time is 0, and $t$ is the resting time. $A_{thix}$ is the thixotropy value in the transient state, $\tau_0$ is the yield stress derived from the Bingham model, and $T$ is the time required for the transient state.

Some studies have focused on the thixotropy and buildability of concrete.
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2.2 Setup of the thixotropy experiment

Various thixotropy measurement methods in the literature were considered to evaluate the buildability of cementitious materials for 3D printing (Roussel et al. 2006, Zhang et al. 2018, Zhang et al. 2019). Fig. 1(a) shows the constructed measurement protocol, where the flow of the material can be changed to the initial state by maintaining the highest shear rate reached over time, and the state of flocculation of the material due to thixotropy can be evaluated by reducing the shear rate [40]. The range of the shear rate was determined by considering the material pumping speed for 3D printing. In general, the shear rate is 20–40 s⁻¹ when concrete is pumped. If cement paste without aggregate is assumed to be homogenous, it has a higher shear rate than concrete (Roussel et al. 2018). The range of the shear rate was determined with \( \gamma_{cp} = \gamma_{concrete}/(1 - \varphi) \), which is based on the correlation between the shear rates of cement paste and concrete (Roussel et al. 2006). Concrete typically has a \( \varphi \) value of approximately 0.8. This shows that cement paste has a shear rate that is five times that of concrete. Thus, the range of the shear rate for measuring thixotropy with cement paste was set to 0-200 s⁻¹. As shown in Fig. 1(a), an experiment was also performed to measure the duration of the maximum shear stress at a maximum shear rate of 200 s⁻¹. The shear stress decreased over time and converged to a value after 600 s, as shown in Fig. 1(b). For the cement paste, a water-cement mixing ratio (W/C) of 0.4 was used considering the consistency of the measurement equipment and experimental values. This enabled measurement even at high shear rates and produced small differences in the results even for repeated experiments.

Table 1 Composition of cement

<table>
<thead>
<tr>
<th>Type</th>
<th>CaO (%)</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>MgO (%)</th>
<th>Fe₂O₃ (%)</th>
<th>SO₃ (%)</th>
<th>LOI (%)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>61.60</td>
<td>19.80</td>
<td>4.50</td>
<td>3.01</td>
<td>3.57</td>
<td>2.10</td>
<td>1.20</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Fig. 2 Rheometer for thixotropy measurement

As shown in Fig. 2, the thixotropy was measured with an Anton Paar rheometer, which has high measurement accuracy in a high shear stress range. To prepare the material, a four-step mixing process was performed in 180 s with a high-speed mixer. First, cement was weighed in a vessel and dry mixed for 60 s. Water was added, and low-speed mixing was performed with a mixing rod for 30 s. Another low-speed mixing period was performed for 30 s, and then a final high-speed mixing period was performed for 60 s. Table 1 presents the chemical composition of the ordinary Portland cement (OPC) used in this study. Distilled water was used to minimize the influence of any impurities on the rheology experiment. A new mixture was prepared for each experiment to evaluate the reliability of the results. The experiment was repeated three times for each case, and the results were averaged. A cylindrical spindle was used.

3. Analysis of thixotropy behavior according to the resting time and derivation of its relationship with buildability

3.1 Thixotropy behavior according to the resting time and its correlation with the model

For concrete, 3D printing is typically performed by additive manufacturing: stacking one layer on top of the previous. The resting time is the time interval between the additive manufacturing of each layer. If the resting time is short and the next layer is stacked when the previous layer is not fully flocculated, it may tilt or collapse in severe cases because it lacks endurance. In this study, the thixotropy behavior was analyzed through a measurement method that uses the resting time as a variable, as shown in Fig. 3. The thixotropy behavior was determined from the area of the hysteresis loop \( (A_{hyst}) \), which is derived through the measurement method in Fig. 3. \( A_{hyst} \) is determined from the difference in integrated areas according to the maximum shear rate

\[
A_{hyst} = \int_0^{t_{max}}(f(x)_{up} - g(x)_{down})\,dx
\]
where \( f(x) \) and \( g(x) \) are functions that represent the up-curve and down-curve parts in Fig. 4.

Fig. 5 shows the measured hysteresis loop according to the resting time. The values of \( A_{\text{Hyst}} \) and the results are presented in Fig. 6 and Table 2. \( A_{\text{Hyst}} \) tended to rapidly increase at first, except when the resting time was 60 s, and converged to a value over time as the rate of increase slowly decreased. The experimental results for a resting time of 60 s were not much different from the results for a resting time of 0 s because the time interval was too short. \( A_{\text{Hyst}} \) converged to a value with a resting time of 600 s as the rate of increase dropped below 2%. This indicates that the state of flocculation of the material converged within the resting time at a certain point.

Based on the above analysis on the thixotropy behavior according to the resting time, a correlation was obtained between the thixotropy behavior and Eq. (4) in Section 2.1. For this, the \( A_{\text{Hyst}} \) of Eq. (4) was derived through \( A_{\text{Hyst}} = \frac{A_{\text{thix}}}{t} \) in Eq. (5). \( t_0 \) in Eq. (5) was derived average 20 Pa by rheological experiment results in Fig. 5. The value \( T \) for the transient state was derived using the measurement protocol as shown in Fig. 7(a). This protocol is designed to measure...
the time to recover equilibrium state after structural break down with high shear rate. As a result, it had recovered to equilibrium after 60 seconds as shown in Fig. 7(b). This led to the result of $T=60$ s. $A_{thst}$ in Eq. (5) was calculated to be 0.34 based on the measurement results. This was classified as in the range of typical thixotropy concrete based on the work of research (Roussel et al. 2006).

To indicate the $\tau_c$ tendency of $\tau_c(t) = \tau_{0c} + A_{thst}t$ in Eq. (4) according to the resting time, the results shown in Fig. 5 were graphed as the shear stress-shear strain curves shown in Fig. 8. Here, $\tau_{0c}$ was set as the value obtained when the rate of increase or decrease for the slope at a resting time of 0 s was less than $\pm 1\%$. $\tau_{0c}$ was used to derive the value of $\tau_c$ according to the resting time, and the results are presented in Table 3. $\tau_c$ tended to rapidly increase at first and converge to a value with a decreasing rate of increase as the resting time increased, similar to $A_{thst}$.

Fig. 9 compares the tendencies of $A_{thst}$ and $\tau_c$ according to the resting time. Both tended to increase at first and converged to a value after a resting time of 600 s. Differences in value were similarly small for short resting times of 0 and 60 s. In other words, both $A_{thst}$ and $\tau_c$ converged when the resting time was above a certain threshold. The relationship between $A_{thst}$ and $\tau_c$ according to the resting time confirmed a strong correlation between the thixotropy measurement method and model.

### 3.2 Thixotropy behavior analysis of the simulated 3D printing additive manufacturing process

During the additive manufacturing process of 3D printing for concrete, the material is pushed through the pressure pipe under continuous shear force until it is discharged from the outlet. After the discharge, the material is freed from the shear force and flocculates as it is stacked. In other words, thixotropy occurs. Fig. 10 shows the experimental method used to analyze the thixotropy behavior of 3D printed concrete after additive manufacturing. To simulate the initial pumping process, a continuous shear force was applied to the material with a shear rate of 200 s$^{-1}$ for 10 s. The shear rate was set to 200 s$^{-1}$ based on the maximum shear rate for the pumping of cement paste, as discussed in Section 2.2. The shear rate was then reduced to close to zero to simulate the additive manufacturing process, and the shear stress of the flocculated material was measured for different resting times. Next, a shear rate of 200 s$^{-1}$ was maintained for 600 s to change the flow of the material back to the initial state. Then, the shear rate was reduced to close to zero (shear rate=0.1 s$^{-1}$), and the buildup of shear stress during the resting time was measured. Here, “buildup” refers to the shear stress recovered by the material due to thixotropy as the flow reverts to the initial state with the high shear rate and then the shear rate is dropped close to zero. The buildup ratio was used to evaluate the degree of recovery through buildup; this is the ratio of the buildup to the stress measured immediately before the flow became the initial state. The reference value for the initial state is expressed as $\tau_{initial}$, and the recovery state of the flow from the initial state due to thixotropy (i.e., buildup value) is expressed as $\tau_{buildup}$. The buildup ratio was determined to be $\tau_{buildup}/\tau_{initial}$. An attempt was made to derive the buildup ratio of the material
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Based on the results of a previous study (Choi et al. 2019), the shear rate for buildup was determined to be 0.1 s\(^{-1}\), at which only the recovered shear stress can be measured without affecting the flow state of the material.

Fig. 11 presents the experimental results according to the resting time. The results were used to derive the buildup ratio according to the resting time, as presented in Fig. 12 and Table 4. As the resting time increased, the buildup ratio rapidly increased at first but converged to a value after a resting time of 600 s as the rate of increase decreased. The rate of increase decreased when the buildup ratio was greater than 1. If the buildup ratio is greater than 1, then \(\tau_{\text{buildup}}\) is greater than \(\tau_{\text{initial}}\). This indicates that the initial shear stress has been completely recovered. In other words, a buildup ratio of 1.07 at a resting time of 600 s indicates that the next layer was stacked when the material completely recovered to its initial shear stress. The results in Fig. 12 indicate that the resting time of the material to secure a sufficient state of flocculation for the previous layer can be derived.

The tendencies of \(A_{\text{floc}}\) and the buildup ratio according to the resting time were compared. As shown in Fig. 13, the

![Fig. 11 Measured thixotropy buildup history according to resting time](image)

![Fig. 12 Buildup ratio according to the resting time](image)
measured values showed similar tendencies for all resting times. In particular, the rates of increase of $A_{\text{Hyst}}$ and the buildup ratio were very similar with a difference of less than 2% at resting times of 300, 600, and 900 s. Here, the buildup ratio represents the recovery capability of the material according to the resting time, which means that the material flocculates by itself. In other words, $A_{\text{Hyst}}$, which represents the state of flocculation, increases as the shear stress is recovered. Therefore, when the buildup ratio exceeded 1 after a resting time of 600 s, $A_{\text{Hyst}}$ also converged to a constant state of flocculation because the initial shear stress was completely recovered. These results confirmed that $A_{\text{Hyst}}$ is affected by the buildup ratio. This indicates that $A_{\text{Hyst}}$ and the buildup ratio have similar tendencies according to the resting time. It also confirms that both parameters are related to the resting time for the 3D printability of concrete.

4. Conclusions

This basic study evaluated the buildability of cementitious materials for 3D printing. The thixotropy behavior in the cement paste step was analyzed according to the resting time. A measurement method was developed that simulates the additive manufacturing process of 3D printing and used to derive a relationship between thixotropy behavior and the 3D printability of concrete. The main results are summarized as follows:

• The thixotropy behavior according to resting time showed that $A_{\text{Hyst}}$ rapidly increased at first and then converged to a value after a specific resting time. This confirmed that the flocculation of the material converged after a certain resting time. Ultimately, the hysteresis loop can be used to determine the resting time for realizing the buildability of concrete.

• Both $A_{\text{Hyst}}$ and $\tau_{\text{r}}$ tended to rapidly increase at first with increasing resting time and then converged to a value after a specific resting time. Both $A_{\text{Hyst}}$ and $\tau_{\text{r}}$ converged at the same time with a specific resting time, which confirms a correlation between the developed thixotropy measurement method and the model.

• When the additive manufacturing process of 3D printing for concrete was simulated, the buildup ratio tended to increase at first and then converged as the resting time increased. A resting time that allows for complete recovery of the material could be determined according to the buildup ratio. This indicates that a resting time for the full recovery of the initial constant flow state can be obtained for the 3D printing of concrete.

• $A_{\text{Hyst}}$ and the buildup ratio tended to increase with the resting time while exhibiting very similar rates of increase at the same resting time. In addition, both $A_{\text{Hyst}}$ and the buildup ratio converged at the resting time for which the state of flocculation of the material was fully recovered. This confirmed that $A_{\text{Hyst}}$ and the buildup ratio are related to the buildability of concrete.

• As a result of the experiment, it was confirmed that the thixotropy index, $A_{\text{Hyst}}$, and buildup ratio showed a close relationship in terms of thixotropy. In addition, these measurement methods are considered to be able to show a close relationship with the buildability of 3D concrete printing in evaluating the flocculation and recovery properties of materials.

• The proposed thixotropy measurement method should be useful for determining the resting time to realize the buildability of concrete. However, the thixotropy behavior was measured under limited material conditions in this study. The proposed measurement method needs to be further verified with various mixing proportions and conditions.

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