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# Citric Acid Influence on Sprayable Calcium Sulfoaluminate Cement-Engineered Cementitious Composites' Fresh/Hardened Properties

by He Zhu, Kequan Yu, and Victor C. Li

Calcium sulfoaluminate cement (CSA) is effective in suppressing drying shrinkage of engineered cementitious composites (ECC). However, the rapid hardening of CSA can shorten the time window for spray applications. In this study, citric acid (CA) was investigated for tuning the fresh properties of CSA-ECC without diminishing the hardened properties. CA was found to mitigate the workability loss and the expansion magnitude of CSA-ECC. While CA had a negligible effect on the strength of ECC at 28 days, the early-age strength decreased noticeably at a high CA dosage. An optimal dosage of a 0.2% binder weight of CA was found to extend the time window for spraying from 40 to 90 minutes while maintaining negligible strength loss and high tensile ductility at 7 days. The rheology tuning approach using CA in combination with CSA can be exploited to support future designs of ECC for different processing methods, including three-dimensional (3D) printing, in addition to spray applications.

**Keywords:** calcium sulfoaluminate (CSA); citric acid (CA); engineered cementitious composites (ECC); expansion; limestone calcined clay cement (LC3); retarder; rheology; spray.

## INTRODUCTION

Engineered cementitious composites (ECC) are a deliberately engineered fiber-reinforced concrete exhibiting strain hardening, and multiple microcracks, and have been demonstrated to be suitable for durable repair applications.<sup>1-3</sup> Sprayable ECC has been developed and applied to infrastructure repair due to its advantages of cost-effectiveness, high construction efficiency, and durability.<sup>2,4</sup> Rheology control is crucial for the sprayability of fresh ECC, which must also maintain the unique characteristics of tensile ductility in the hardened state.

Rapid-hardening cement is usually adopted in sprayable ECC to obtain a two-stage rheology development, maintaining high flowability before spraying but fast thickness buildup ability on a substrate.<sup>5</sup> Moreover, the shrinkage of ECC can be up to 1500 to 2000  $\mu\epsilon$  due to the elimination of coarse aggregates in ECC composition,<sup>6,7</sup> leading to potential restrained shrinkage cracking. Calcium sulfoaluminate cement (CSA) has received increasing attention for sprayable ECC because CSA has the dual advantages of fast setting and shrinkage compensation.<sup>8-10</sup> CSA has demonstrated good strength and ductility performance in ECC, such as the high-early-strength ECC,<sup>11,12</sup> low-shrinkage ECC,<sup>7</sup> and expansive ECC.<sup>13</sup> Particularly, a low-carbon sprayable ECC has been developed using CSA and limestone calcined clay cement (LC3),<sup>14</sup> where the synergistic effect

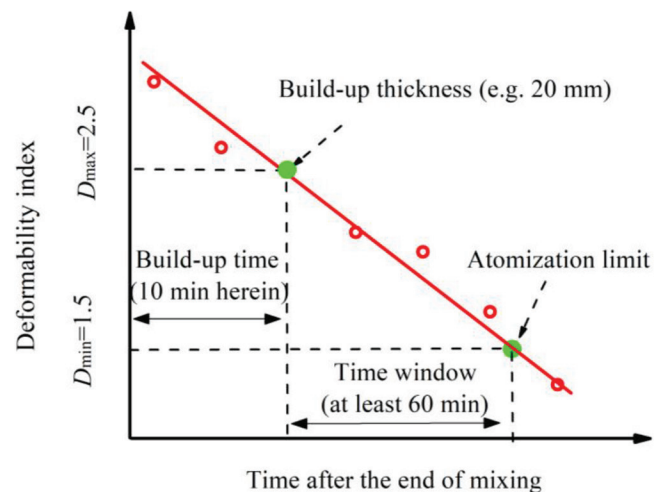


Fig. 1—Schematic experimental data showing decay of deformation with time after mixing, and definition of sprayable time-window and buildup time.

of CSA and LC3 assures the advantage of buildup thickness and expansive ability, as well as material greenness.<sup>3</sup> However, the increased CSA dosage for expansion shortens the working time for spraying (under 30 minutes) because of the rapid-hardening characteristics.<sup>9</sup> The rapid flowability loss hinders the wider application of the CSA. Therefore, it is imperative to extend the setting time of CSA-ECC, as well as to maintain the sprayability, to meet the requirement of adequate working time in practical applications.

The setting time of CSA can be prolonged 1 to 10 hours, compared to the setting time of ordinary portland cement (OPC),<sup>15</sup> by various retarder admixtures, such as tartaric acid, sodium gluconate, and sodium borate.<sup>16-19</sup> Among potential retarders, the effectiveness of citric acid (CA) has been demonstrated in a pure CSA system,<sup>9,20,21</sup> a CSA-OPC blended system,<sup>22,23</sup> and a limestone-CSA system.<sup>24</sup> Therefore, CA is selected as the retarder herein for controlling the spray time of ECC, of which the cement system includes OPC, CSA, and limestone.<sup>14</sup>

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**Table 1—Chemical compositions of OPC, CSA, FA, and MK, %**

| Material | CaO  | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | SO <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO  | Others |
|----------|------|--------------------------------|------------------|-----------------|--------------------------------|------|--------|
| OPC      | 63.5 | 4.8                            | 19.6             | 2.6             | 2.9                            | 2.2  | 4.4    |
| CSA      | 47.2 | 10.1                           | 7.0              | 33.1            | 0.7                            | 1.1  | 0.8    |
| FA       | 17.4 | 19.8                           | 39.4             | 1.9             | 11                             | 3.70 | 6.8    |
| MK       | 0.0  | 46.6                           | 50.8             | 0.1             | 0.5                            | 0.0  | 2.0    |

Fresh properties are crucial for sprayable ECC, which can be controlled through a deformability index (defined in the section “Fresh property test”).<sup>14</sup> As shown in Fig. 1, the fresh ECC requires a fast buildup ability on a substrate—for example, more than 20 mm in 10 minutes<sup>14</sup>—corresponding to the upper bound of the deformability index ( $D_{max}$ ). During the spray process, the fresh ECC sprayed from the nozzle should be atomized (broken up into small particles) so that the fibers disperse evenly—that is, inadequate atomization decreases the hardened mechanical performance of sprayable ECC due to poor fiber dispersions,<sup>14</sup> thus setting a lower limit of the deformability index ( $D_{min}$ ). The spraying time window, restrained by  $D_{max}$  and  $D_{min}$ , is preferred to be at least 60 minutes in practical applications.<sup>4,5,18</sup> The fresh properties of cementitious materials, such as the flowability and setting time, can be tailored by varying the CA dosages.<sup>16,25,26</sup> However, to the best knowledge of the authors, there has been no study on the effect of CA on sprayable ECC. When CA is employed as a retarder to mitigate the flowability loss of the sprayable ECC, the fresh properties’ development must be carefully examined to meet the requirement for buildup thickness, spray operating time, and atomization quality (fiber dispersion).

In addition to influencing the fresh properties, CA may also influence the hardened properties of ECC, including strength, shrinkage/expansion, and tensile ductility. No consensus has been reached regarding the influence of CA on the strength development of cementitious materials. Some literature reported that the compressive strength decreased at early age (1 to 7 days), but could be restored to a level comparable to that without CA at 28 days or later.<sup>26,27</sup> However, the reduction of both the early and later (up to 90 days) strength was also reported.<sup>28,29</sup> Furthermore, a loss of strength over time was reported,<sup>9</sup> in which the 28-day compressive strength is lower than that at 7 days. A reduction in compressive strength of the OPC and CSA blended system at later ages was also found in the literature.<sup>30</sup> Therefore, the influence of CA on the strength appears to depend on the type of cement, hydration stages, and retarder contents. In contrast to compressive strength, no report on the influence of CA on the tensile ductility of ECC is found in the literature. Research is needed on the effects of CA on the strength and ductility of CSA-based ECC.

This research aims at extending the sprayable time of CSA-based ECC while maintaining the advantages of good atomization quality (for achieving high fiber dispersion), no strength reduction, and ultra-high tensile strain capacity. CA was employed to work as a retarder in 0 to 0.5% by weight of the binder. The flowability was measured by the flow table per ASTM C1437,<sup>31</sup> and the sprayability was checked with a spray hopper. The drying expansion/shrinkage, compressive

strength, and uniaxial tensile test were conducted to investigate the effect of CA on the mechanical performance of ECC.

## RESEARCH SIGNIFICANCE

Sprayable ECC has been demonstrated as a promising material for infrastructure repair. Furthermore, CSA is employed in the sprayable ECC for buildup thickness and shrinkage compensation purposes. However, the shortened working time caused by the rapid hardening of CSA impedes its application. Though CA has proven successful in prolonging the setting time of the CSA cement, knowledge on its effects on the sprayability and hardened properties of ECC, especially the tensile ductility, is lacking. This research aims at filling this knowledge gap, critical to the appropriate use of CA in sprayable ECC, to extend the sprayable time window while maintaining the mechanical performance.

## EXPERIMENTAL INVESTIGATION

### Materials

The binder system of the ECC composition includes OPC (Type I), a CSA additive, metakaolin (MK), limestone (LS), and fly ash (FA). The commercially available binder ingredients have chemical compositions as listed in Table 1. The particle size distribution of the binder ingredients can be found in Zhu et al.<sup>3</sup> A ready-to-use high-range water-reducing admixture is employed as the water reducer (WR). CA (Anhydrous, 99% purity) is used for tuning the setting time of the sprayable ECC. The polypropylene (PP) fiber has a 12  $\mu$ m diameter, 10 mm length, 6 GPa Young’s modulus, and 850 MPa tensile strength.

To prepare the ECC, dry ingredients were pre-mixed with a weight ratio of CSA:OPC:MK:LS:FA = 0.42:0.13:0.30:0.15:2.2. After mixing in a 5.6 L mixer at 100 rpm for 10 minutes, tap water (0.3 weight of the binder) associated with WR and CA were added into the dry materials, which were further mixed for 5 minutes at 100 rpm. A 2% volume of PP fibers were subsequently added into the fresh materials, which were further mixed at 150 rpm for 6 minutes. WR contents of 0.35, 0.50, 0.65, and 0.80% weight of the binder were adopted to study the initial flowability for sprayable ECC. CA with an amount of 0.1, 0.2, 0.3, and 0.5% weight of the binder was employed to extend the time window for spraying. These compositions were tested for their fresh properties and mechanical performance, as summarized in Table 2 and with test details given in the following.

### Fresh property test

The flow table (diameter  $d_0 = 10$  cm) test per ASTM C1437<sup>31</sup> has been demonstrated as a practical tool for measuring the sprayability of ECC.<sup>14</sup> After dropping the

flow table 25 times in 15 seconds, the maximum spread diameter ( $d_1$ ) and the diameter perpendicular to  $d_1$  (marked as  $d_2$ ) (Fig. 2) were recorded and used for calculating the deformability index ( $D$ )<sup>5</sup> as follows

$$D = \frac{(d_1 \times d_2) - d_0^2}{d_0^2} \quad (1)$$

The deformability index ( $D$ ) can be adopted as a criterion for the sprayability of ECC by Zhu et al.,<sup>14</sup> where  $D_{max}$  and  $D_{min}$  were proposed as 2.5 and 1.5, respectively. Different water-reducer (WR#) contents (WR0.35-C0, WR0.50-C0, WR0.65-C0, and WR0.80-C0) and CA (C#) dosages (WR0.65-C0, WR0.65-C2, and WR0.65-C5) were used for the flowability test, to tailor the buildup time and spray operating time. Further, a spray hopper connected with a 500 kPa air system (Fig. 3) was used for validating the relationship of the sprayable time window and deformability index, as proposed by Zhu et al.<sup>14</sup>

### Mechanical performance test

To study the effect of the CA dosage on the hardened mechanical performance, the mixtures WR0.65-C0, -C1, -C2, -C3, and -C5 were employed for the expansion/shrinkage measurement per ASTM C490-17,<sup>32</sup> compressive



Fig. 2—Flow table test of fresh ECC.

strength per ASTM C109-20,<sup>33</sup> and uniaxial tension tests (Table 2). Prism specimens (25 x 25 x 300 mm in Fig. 4(a)), 50 mm cube specimens,<sup>33</sup> and dogbone-shaped specimens (Fig. 4(b))<sup>3</sup> were employed for the expansion/shrinkage, compressive strength, and tensile tests, respectively. The uniaxial tensile test was conducted on a servo-hydraulic system at a rate of 0.5 mm/min<sup>3</sup>. The deformation was measured by two linear variable displacement transducers (LVDTs) with an 80 mm gauge length. Specimens were stored in a 20 ± 3°C and 40 ± 5% relative humidity (RH) environment. Three specimens for each mixture (Table 2) were tested per batch.

The expansion/shrinkage measurement starts immediately after specimen demolding until 28 days and is designed for hardened deformation determination without damaging the specimen.<sup>14</sup> The earliest demolding time was at 3, 4, 4.5, and 5 hours for the mixtures WR0.65-C0, -C1, -C2, -C3, and -C5, respectively. The compression and tension tests were conducted at age 1, 3, 7, and 28 days to quantify the effect of CA on strength development.

## RESULTS AND DISCUSSION

### Fresh properties

The WR significantly influences the flowability of ECC quantified by the deformability index  $D$  in Fig. 5. A higher WR content leads to a higher initial deformability, while the flowability loss rate with time is negligible for the range of WR dosages in this study—that is, the fresh ECC has a similar flowability loss as a function of time regardless of the

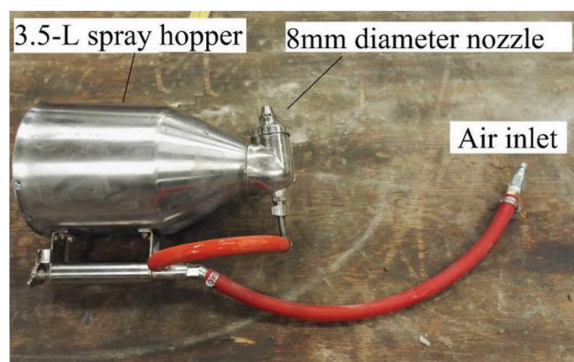


Fig. 3—Spray hopper used for buildup thickness tests.<sup>14</sup>

**Table 2—Fresh and hardened property tests conducted for various ECC mixtures**

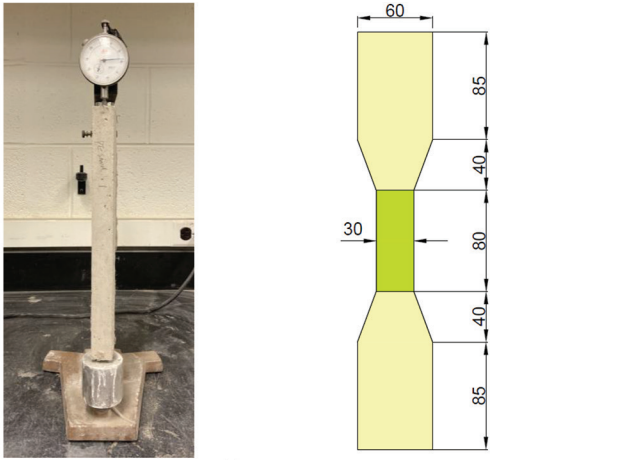
| Mixture   | WR*  | CA† | Flowability | Sprayability | Shrinkage | Compression | Tension |
|-----------|------|-----|-------------|--------------|-----------|-------------|---------|
| WR0.35-C0 | 0.35 | 0   | ×           | —            | —         | —           | —       |
| WR0.50-C0 | 0.50 | 0   | ×           | —            | —         | —           | —       |
| WR0.65-C0 | 0.65 | 0   | ×           | ×            | ×         | ×           | ×       |
| WR0.80-C0 | 0.80 | 0   | ×           | —            | —         | —           | —       |
| WR0.65-C1 | 0.65 | 0.1 | —           | —            | ×         | ×           | ×       |
| WR0.65-C2 | 0.65 | 0.2 | ×           | ×            | ×         | ×           | ×       |
| WR0.65-C3 | 0.65 | 0.3 | —           | —            | ×         | ×           | ×       |
| WR0.65-C5 | 0.65 | 0.5 | ×           | ×            | ×         | ×           | ×       |

\*WR is water reducer, weight % of binder.

†CA is citric acid, weight % of binder.

Note: — are not measured items; × are measured items.





(a) The setup of the shrinkage/expansion test. (b) Dimension of dogbone specimen with 13-mm thickness (Units in mm).

Fig. 4—Shrinkage/expansion specimen and dogbone-shaped specimen for uniaxial tension test.

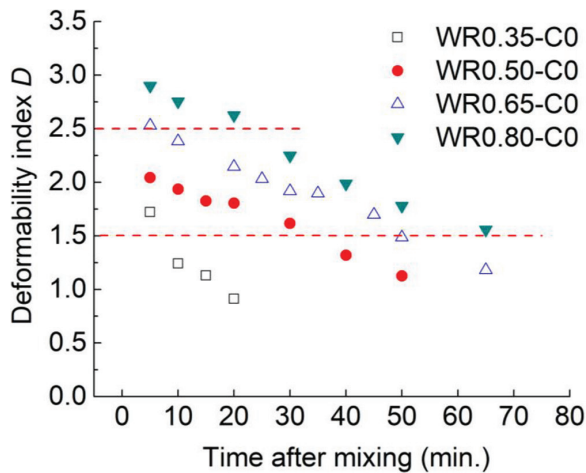


Fig. 5—Influence of WR on flowability decay behavior of ECC, without CA.

WR dosages. As proposed by Zhu et al,<sup>14</sup> the deformability index should be controlled between 1.5 to 2.5. The  $D_{min} = 1.5$  is the minimum deformability index limit for assuring the atomization quality, which in turn influences the mechanical performance of the sprayed ECC. The  $D_{max} = 2.5$  is the maximum deformability limit index for buildup thickness, above which the ECC cannot build up on the substrate. The initial deformability of WR0.30-C0 and WR0.50-C0 is too low, leading to the atomization quality that cannot be fulfilled beyond 10 minutes and 30 minutes, respectively. An excessive amount of WR results in an initial flowability so high that the WR0.80-C0 could not meet the buildup requirement before 30 minutes. Hence, a 0.65% weight of the binder was chosen as the optimal WR content for the sprayable ECC to obtain a moderate flowability.

With the addition of CA, the hydration of the ECC binder is significantly retarded (Fig. 6). The deformability index decreases almost linearly with time for WR0.65-C0, while its development with time for WR0.65-C2 and WR0.65-C5 shows three distinct stages. The initial deformability is decreased slightly by the CA addition, while the second stage is prolonged by increasing the CA dosage (40 minutes

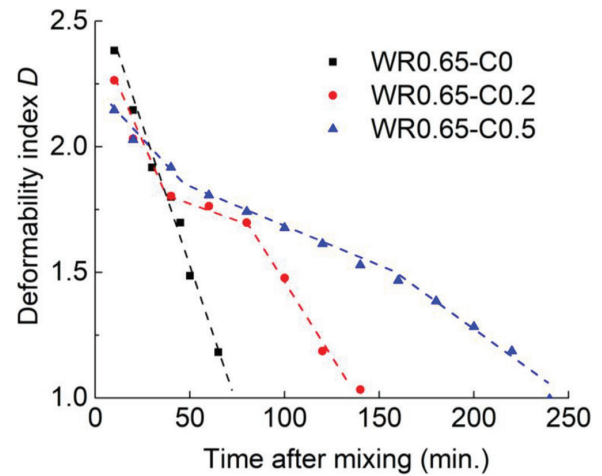


Fig. 6—Influence of CA on flowability decay behavior of ECC, at fixed WR of 0.65 weight % of binder.

for WR0.65-C2 and 110 minutes for WR0.65-C5). Although the deformability loss is accelerated in the third stage, WR0.65-C5 retains a lower loss rate than WR0.65-C2 and WR0.65-C0. Therefore, CA can effectively prolong the setting time and prevent the rapid hardening of CSA-ECC.

Although the mechanism of how CA influences the hydration kinetics has not been fully understood,<sup>9</sup> it has been attributed to the inhibition of clinker dissolution and/or hydrates precipitation.<sup>17</sup> The adsorption theory is one of the most accepted retardation mechanisms of CA on CSA. Citrate sorbs on the surface of cement grains form a protective layer and inhibit the dissolution of ye'elimit and precipitation of the ettringite.<sup>15,17,28,34</sup> The competitive adsorption effect between CA and WR accounts for the decrease of initial deformability, consistent with the finding in Zhang et al.<sup>29</sup> The suppression of ettringite precipitation increases the dormant period of hydration kinetics,<sup>9</sup> resulting in the prolonging of the second stage under the presence of CA. A higher dosage of CA yields a longer duration of the second stage. An acceleration period, corresponding to the peak of the hydration heat release,<sup>9,18,35,36</sup> emerges following the dormant period, concurrent with the third stage of deformability evolution. By modulating the flocculation rate of cement grains,<sup>5</sup> the deformability loss versus time is changed from a linear decrease to the three-stage development shown in Fig. 6. In particular, the second stage is prolonged, which is beneficial for extending the spray time window of ECC.

The relationship of sprayability and flowability is further validated in Fig. 7, which shows the influence of CA content and time after mixing on the buildup thickness of sprayed CAS-ECC. The buildup thickness at 10 minutes can reach at least 20 mm for WR0.65-C0, WR0.65-C2, and WR0.65-C5 because their initial deformability indexes were all smaller than 2.5 at 10 minutes. The reduction of the initial flowability caused by CA does not affect the buildup ability of ECC. The reference mixture without CA (WR0.65-C0) has a deformability index below 1.5 at 60 minutes and cannot be sprayed out evenly (Fig. 7(b)).

Based on the proposed deformability range of 1.5 to 2.5,<sup>14</sup> the buildup time and time window (Fig. 1) for spraying have been experimentally determined for the various mixtures

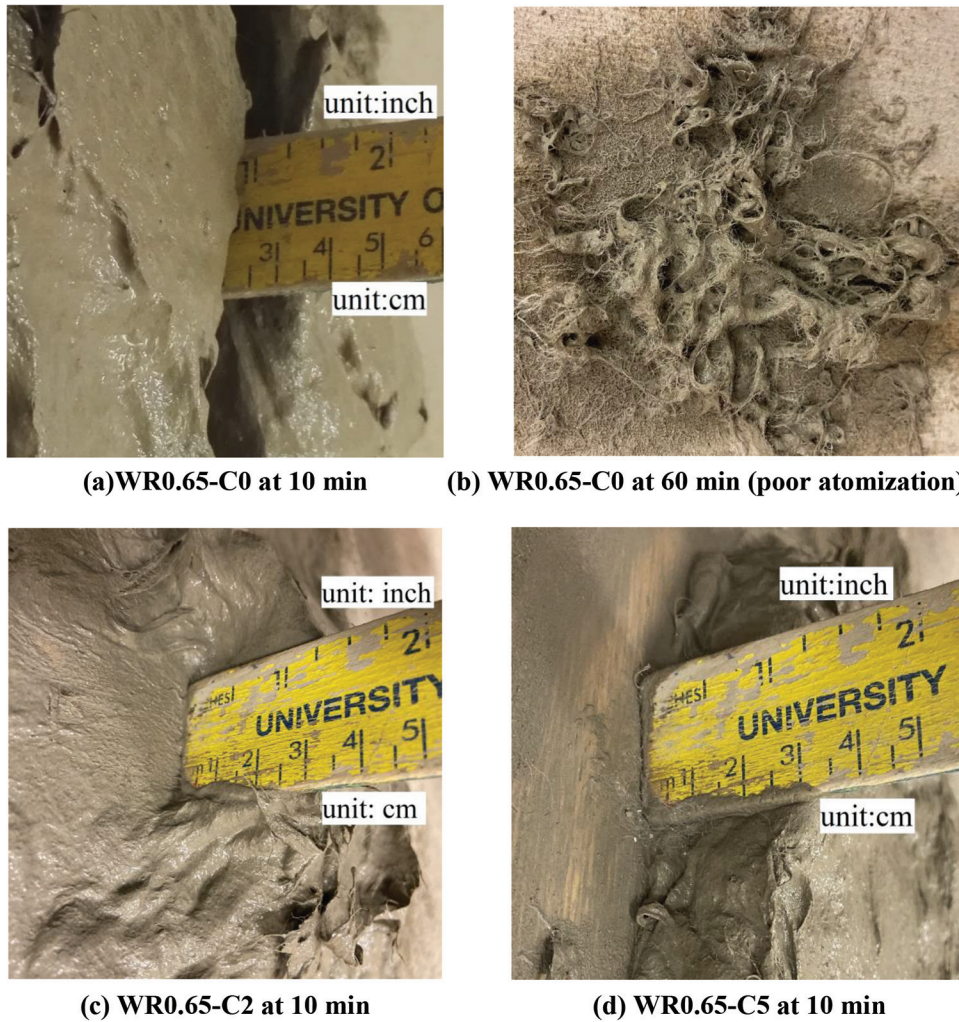


Fig. 7—Buildup thickness and atomization quality of sprayable ECC.

and are shown in Fig. 8. Increasing the WR content prolongs the buildup time due to the high initial flowability. The time window is extended from 5 to 40 minutes when the WR content increases from 0.35 to 0.65% weight of the binder. However, a further increase in the WR—for example, WR0.80-C0, does not extend the time window of 40 minutes, but results in a delay of the buildup time by 15 minutes (from 10 to 25 minutes) when compared with WR0.65-C0.

With a combined use of WR and CA, the buildup time can be maintained while the time window is significantly extended (Fig. 8). The time window for spraying is 90 minutes for WR0.65-C2 and 150 minutes for WR0.65-C5, meeting the requirement of most field applications.<sup>5,9</sup> Hence, adopting CA at 0.2 to 0.5% by weight of the binder provides a sufficient time window for spraying.

In the following section, the expansion/shrinkage behavior and mechanical performance of these mixtures are presented and analyzed.

### Mechanical performance

**Expansion/shrinkage**—The influence of CA on the expansion/shrinkage of the sprayable ECC is investigated (Fig. 9), with characteristic values tabulated in Table 3. Because CA retards hydration at early age, the beginning time of the expansion/shrinkage measurements of the specimens—that

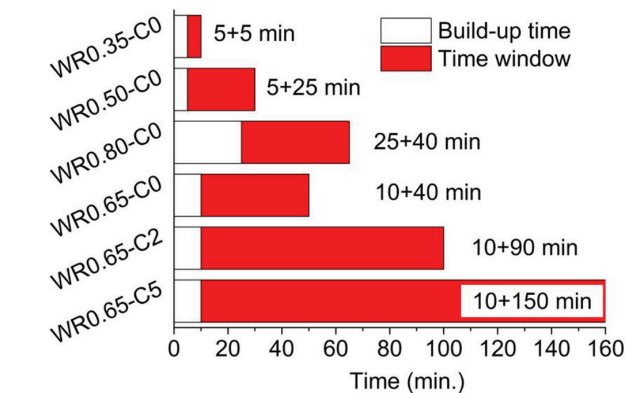


Fig. 8—Buildup time and time window of sprayable ECC tailored by WR and CA.

is, the earliest allowable demolding time, is delayed with an increase in CA content in ECC composition. Under dry-curing in air, the CSA-ECC expanded first, followed by a reversal in expansion. The peak expansion occurred within 1 to 2 days; an increased CA dosage delayed the age of this peak. For example, the peak expansion of WR0.65-C0 was at 31 hours, while that of WR0.65-C5 was at 46 hours. In addition to the time delay, the maximum expansion value was considerably reduced by the introduction of CA. For



**Table 3—Summary of specimen length change influenced by citric acid dosages**

| Material  | Demolding time, hours | Peak expansion time, hours | Maximum expansion, $\mu\epsilon$ | 28-day expansion, $\mu\epsilon$ |
|-----------|-----------------------|----------------------------|----------------------------------|---------------------------------|
| WR0.65-C0 | 3.0                   | 31                         | 2226                             | 1511                            |
| WR0.65-C1 | 4.0                   | 31                         | 1578                             | 603                             |
| WR0.65-C2 | 4.0                   | 43                         | 1149                             | 273                             |
| WR0.65-C3 | 4.5                   | 43                         | 500                              | -212                            |
| WR0.65-C5 | 5.0                   | 46                         | 337                              | -457                            |

Note: Positive value represents expansion, while negative value means shrinkage.

example, the maximum expansion of WR0.65-C5 was only 337  $\mu\epsilon$  compared to 2227  $\mu\epsilon$  of WR0.65-C0. After 2 days, all mixtures have a similar trend of expansion loss. Although the 28-day length change of WR0.65-C0 was 1511  $\mu\epsilon$ , the addition of just a 0.2% binder weight of CA reduced the expansion to 273  $\mu\epsilon$ . WR0.65-C3 and WR0.65-C5 revealed shrinkage (negative value in Table 3) at 28 days.

The expansion of the CSA cement is mainly caused by the formation of ettringite.<sup>8,37</sup> The hydration of CSA may react per Eq. (2) through (6),<sup>9</sup> depending on the sulfate source and calcium hydroxide.



where  $C_4A_3\bar{S}$ ,  $AH_3$ ,  $C_3A \cdot C\bar{S} \cdot H_{12}$ , and  $C_3A \cdot 3C\bar{S} \cdot H_{32}$  represent ye'elimite, aluminum hydroxide, monosulfate, and ettringite, respectively. The sulfate source of anhydrite, bassanite, and gypsum is expressed as  $C\bar{S}$ ,  $C\bar{S}_{0.5}$ , and  $C\bar{S}_2$ . In the absence of sulfate, monosulfate, rather than ettringite, is the main phase of the hydrates (Eq. (2)), where no expansion would be found.<sup>8</sup> In the presence of calcium sulfate (Eq. (3) through (5)), more ettringite is produced, resulting in larger expansion. Due to the slower dissolution of anhydrite compared to bassanite and gypsum, the reaction rate of Eq. (5) is faster than Eq. (4) and (3). If calcium hydroxide is present (Eq. (6)), more ettringite can form. Consequently, more expansion is generated.

The observed diminished expansion caused by CA is consistent with that reported by Coppola et al.<sup>18</sup> The sprayable ECC adopts both OPC and CSA in the cement system. The potassium-citrate that sorbs onto the OPC clinker surface forms a protective layer, which slows down the dissolution of clinker grains<sup>23</sup> and inhibits the nucleation and growth of CH.<sup>35</sup> Citrate sorbed onto the clinker surface forms a protective layer around the surface of the CSA grains, delaying the

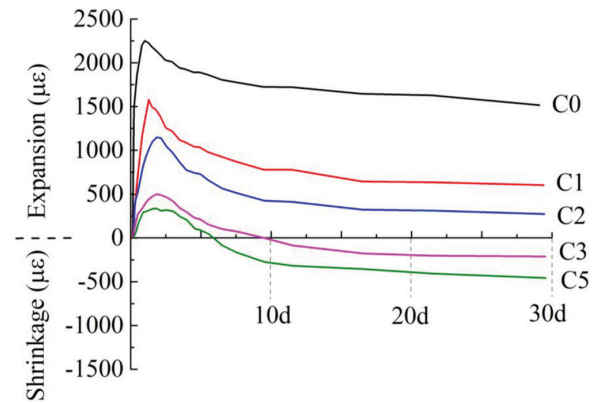


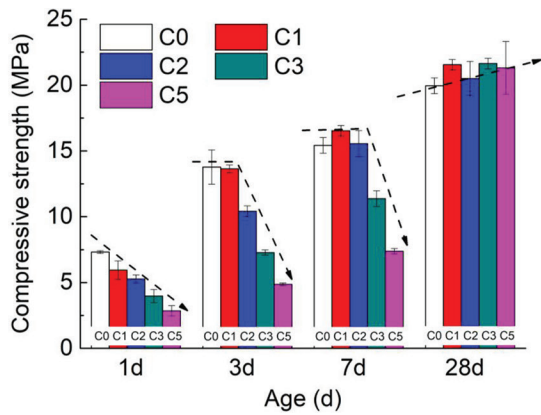
Fig. 9—Influence of citric acid on length change of ECC prism specimens.

dissolution of the main components' ye'elimite.<sup>27,28</sup> Due to the affinity of  $COO^-$  for  $Ca^{2+}$  ions, the CA retards the dissolution of  $C\bar{S}$  and further inhibits the hydration from  $C\bar{S}$  to  $C\bar{S}_{0.5}$ , and  $C\bar{S}_2$ ,<sup>38</sup> resulting in a slower reaction rate of Eq. (3) compared to that governed by Eq. (4) and (5).<sup>38-40</sup> Delayed hydration of  $C\bar{S}_2$  accounts for the delayed demolding time and the time at peak expansion (Table 3). In the absence of  $C\bar{S}$ ,  $C\bar{S}_{0.5}$ , and  $C\bar{S}_2$ , less ettringite is produced. The synergy of diminished reactants (ye'elimite, sulfate, and CH) caused by the retardation effect of CA results in a reduced amount of ettringite and expansion.

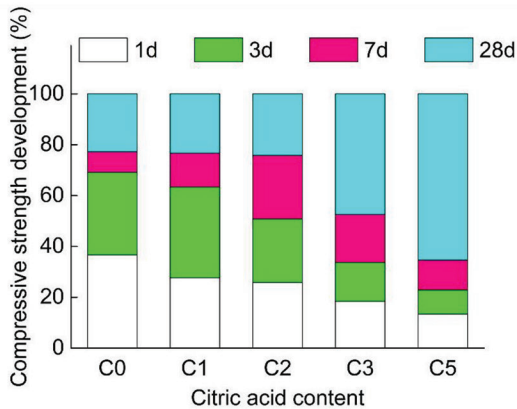
**Compressive strength**—The compressive strength is reduced notably in the early days (before 7 days), particularly on the first day. The reduction degree is proportional to the CA content (Fig. 10(a)). However, the reduction effect is mitigated at later ages. For example, WR0.65-C1's compressive strength at 3 days is comparable to WR0.65-C0, and WR0.65-C2 exhibits no strength retardation at 7 days. At a higher CA content, suppressed compressive strengths at 7 days can be observed in WR0.65-C3 and WR0.65-C5. At 28 days, no retardation effect can be detected in any of the mixtures studied, and the compressive strength is actually slightly increased in the presence of CA.

Normalizing the compressive strength based on the 28-day strength reveals the strength gain over time for the five mixtures (Fig. 10(b)). For the reference mixture without CA (WR0.65-C0), 38% of the compressive strength is gained during the first day, and strength increases to 70% at 3 days compared to 28 days. With the increase of the CA ratio, the strength of ECC develops slower before 7 days, while experiencing a rapid augmentation at a later age. The strength evolution of WR0.65-C5 is considerably suppressed before 7 days, but then gains more than 60% of its strength between 7 and 28 days.

The influence of CA on compressive strength is known to depend on the composition of the binder. For pure CSA, the hydration rate is so dramatic that the setting may occur within 10 minutes, which can be extended to approximately 200 minutes by CA.<sup>9</sup> The compressive strength at a later age is also enhanced when CA is used. However, a strength reduction with time is found when employing a large dosage of CA.<sup>21,29</sup> While the OPC-CSA system exhibits a different strength development, the early age strength is decreased



(a) The compressive strength development versus time.



(b) The relative strength gain rate by normalized strength based on 28 d.

Fig. 10—Compressive strength of ECC with different citric acid contents.

significantly with the addition of CA.<sup>18</sup> However, the retardation effect disappears at a later age; for example, the 28-day compressive strength is comparable for the composition without CA.<sup>18</sup> The retardation effect of CA is more prominent on OPC than on CSA<sup>30</sup>; also, the existence of limestone powder enhances the retardation efficiency of CA on CSA,<sup>24</sup> accounting for the significant reduction of compressive strength of the sprayable ECC at early age (Fig. 10). Unlike the strength loss at later age reported in the literature,<sup>29</sup> no compressive strength regression versus age is found in this study.

**Tensile strength and ductility**—The addition of CA does not appear to negatively influence the tensile strain-hardening behavior of ECC at both 7 and 28 days (Fig. 11 and 12) for all five mixtures studied, which show high ductility. Their tensile strength and strain capacity are summarized in Fig. 13.

For WR0.65-C0 without CA, the first crack strength  $f_o$  is 1.5 MPa at 7 days and increases slightly to 1.7 MPa at 28 days. Also, the ultimate tensile strength  $f_t$  is approximately 2.8 to 2.9 MPa, reached at 7 days due to the rapid-hardening property of CSA. With the incorporation of CA, the first crack strength and ultimate tensile strength are decreased remarkably. The first crack strength of WR0.65-C5 is only 65% of WR0.65-C0; the ultimate tensile strength is also decreased by 25% at 7 days. At a lower CA content—for example, for WR0.65-C2, the effect of CA on  $f_o$  and  $f_t$  becomes negligible

at 28 days. Thus, the impact of the CA addition on the tensile strength at 28 days (Fig. 13(a)) is similar to that on compressive strength at 28 days (Fig. 10).

Figure 13(b) illustrates the tensile strain capacity of ECC. The tensile strain capacity exceeds 5% regardless of the CA dosage or age (7 or 28 days). The high tensile ductility and the robust strain-hardening behavior observed (Fig. 11 and 12) suggest that the addition of CA has a negligible impact on the fiber dispersion or fiber-bridging properties of ECC.

## FURTHER RESEARCH

The sprayable ECC with the CA addition shows promise in infrastructure repair. While the mechanical performance before 28 days has been studied, the durability of this composite, including the long-term shrinkage, strength, and tensile ductility, remains to be investigated. The research of durability would directly benefit the broad application of ECC in infrastructure repair.

## SUMMARY AND CONCLUSIONS

Citric acid (CA) has been demonstrated as an effective admixture in the calcium sulfoaluminate (CSA)-based sprayable engineered cementitious composites (ECC) for extending the spraying time window. The influence of CA on the fresh and hardened properties of ECC has been investigated. The following conclusions can be drawn:

1. The rheology of CSA-based ECC can be modulated by combining the use of a water reducer (WR) and CA. The water-reducer dosage influences the initial flowability, which determines the buildup ability of the sprayable ECC on the substrate. The water-reducer content has little effect on the rate of the loss of flowability, and therefore cannot be used to extend the time window of spraying. The addition of CA, however, shows a strong influence on the flowability loss (as measured by deformability loss in this study) behavior, with minimal impact on the buildup time. CA transforms the flowability-time relation from a linear decay to a three-stage development. The extension of the second stage, approximately 50 minutes when the CA dosage was a 0.2% binder weight, desirably prolongs the time window of spraying.

2. CA mitigates the maximum expansion of CSA-based ECC but has little effect on the subsequent shrinkage (or expansion loss). An excessive amount of CA addition (over a 0.2% binder weight) does lead to a change from expansion to shrinkage at a later age.

3. CA suppresses the strength development of ECC at early age but has a negligible negative effect at later age. With the addition of a 0.5% binder weight of CA, the compressive strength was reduced by 60% at 1 day. The suppression in strength gain at early age increases with the CA dosage. The 28-day compressive and direct tensile strength of ECC, however, appear not to be influenced by the CA dosage.

4. CA has a negligible impact on the tensile strain-hardening behavior of ECC. The tensile strain capacity at 7 and 28 days maintains over 5% for all the ECC mixtures studied, regardless of CA content.

5. Based on this study, a 0.2% binder weight of CA is suggested as the optimum dosage for sprayable ECC. The time window of spraying is extended from 40 to 90 minutes,

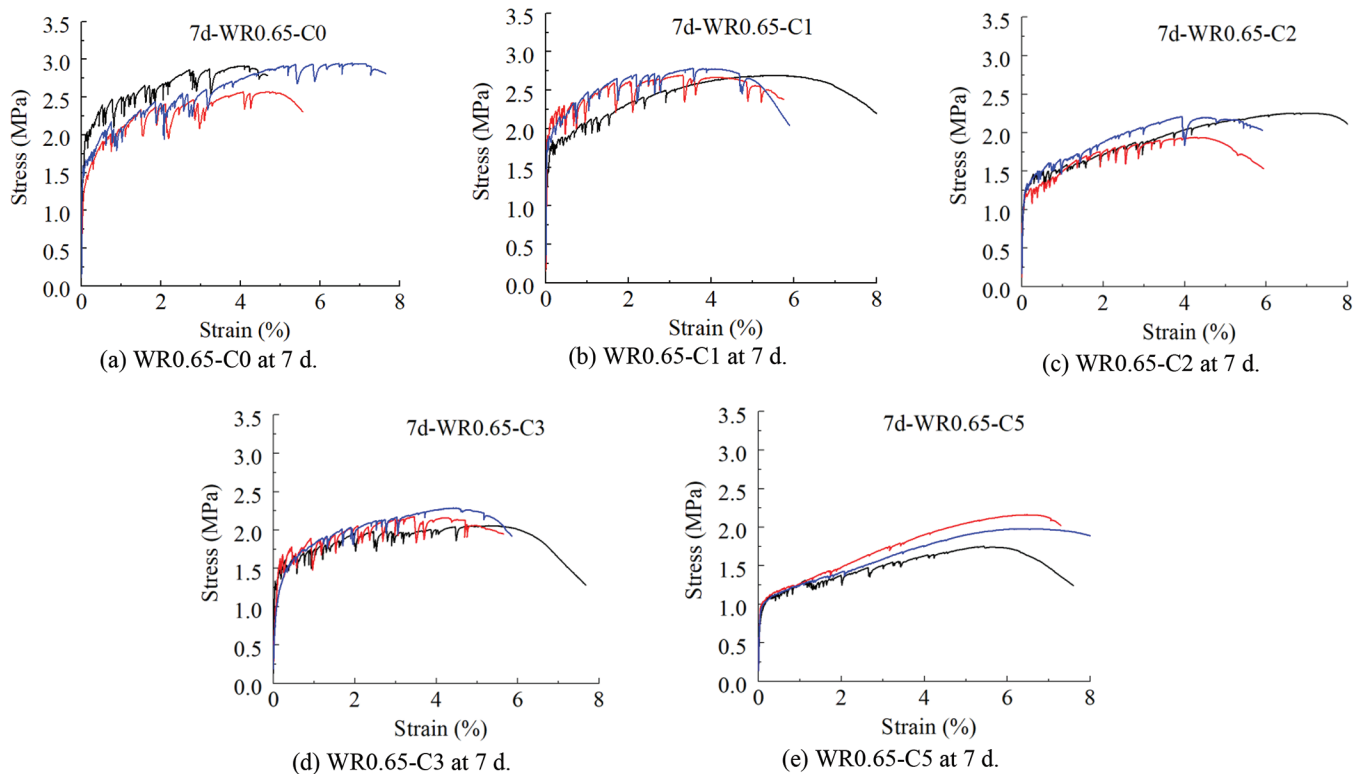


Fig. 11—Uniaxial tensile behavior at 7 days with different citric acid contents.

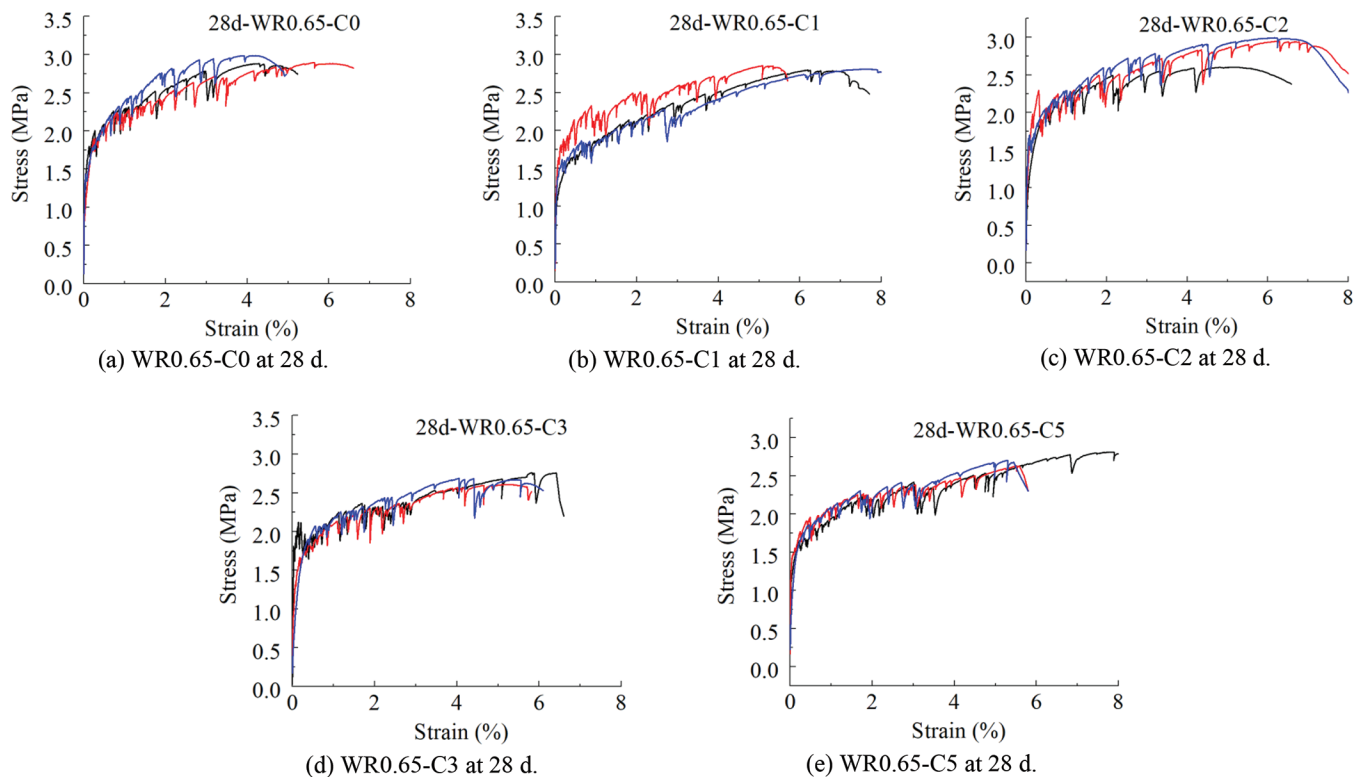
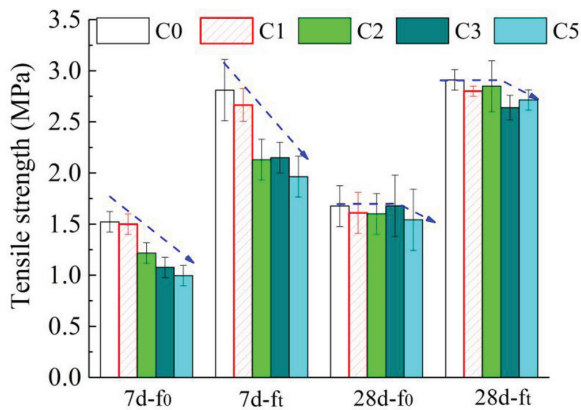
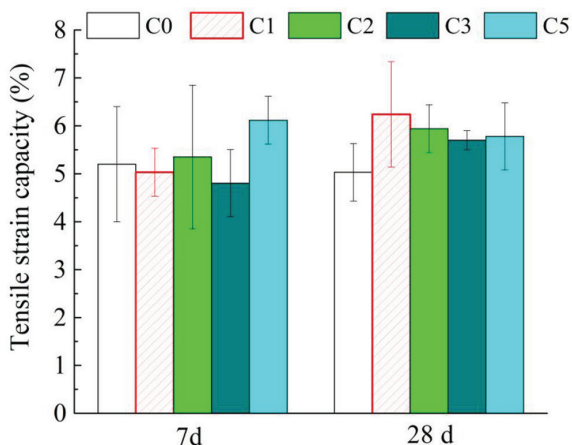


Fig. 12—Uniaxial tensile behavior at 28 days with different citric acid contents.





(a) Tensile strength at 7 d and 28 d.  $f_0$  is first crack strength and  $f_t$  is ultimate tensile strength.



(b) Tensile strain capacity at 7 d and 28 d.

Fig. 13—Tensile performance of ECC under effect of citric acid.

assuring sufficient field operation time while retaining good atomization quality. The sprayable ECC containing a 0.2% binder weight of CA maintains expansion at 28 days so that the shrinkage-free ECC would be more durable. For this mixture, the retarder effect of CA on the mechanical performance is negligible after 7 days.

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