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Engineered Cementitious Composites (ECC) with limestone calcined clay cement (LC³)



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ABSTRACT

Recent research have recognized that coupled use of calcined clay, limestone and cement clinker in concrete is viable to reduce environmental footprints at manufacture and to enhance material durability. In this study, a novel application of the limestone calcined clay cement (LC^3) is demonstrated by substituting the Ordinary Portland Cement (OPC) in Engineered Cementitious Composites (ECC). The composite mechanical properties including σ - δ and σ - ϵ relationships and residual crack widths were evaluated to 28 days under uniaxial tension. Matrix chemistry was characterized using thermogravimetric analysis and X-ray diffraction, while the pore structure of matrices and composites was analyzed using mercury intrusion porosimetry. The LC^3 -based ECC showed more rapid early strength development but lower 28-day strength (~32 MPa) due to a 20% higher water-to-solid ratio for attaining adequate workability and fiber dispersion. Nevertheless, the tensile strain capacity of LC^3 -based ECC achieved over 6% with an average residual crack width less than 50 µm. Additionally, the composite pore structure exhibited a decreasing volume fraction of large pores and voids (>100 nm) after substituting LC^3 for OPC. The use of LC^3 -based ECC shows promise as a greener ductile concrete compared with OPC-based ECC.

1. Introduction

As the world's most used construction material, Portland cement (PC) has been widely recognized as an energy and carbon intensive material, contributing more than 5% of global anthropogenic CO_2 emissions [1]. About 0.9 tonne of CO_2 is emitted for producing 1 tonne PC, mainly due to the high clinkering temperature (~1450 °C) associated with the large consumption of fossil fuels, together with the calcination of limestone as an essential raw material. The desire for mitigating energy and CO_2 footprints of PC-based materials promotes the use of Supplementary Cementitious Materials (SCMs) as partial PC substitution. Along this line, the geographically abundant kaolinite clay shows a high pozzolanic potential after calcination at 600–800 °C, which produces metakaolin as an excellent alternative SCM [2,3]. Fine limestone powders, on the other hand, has been widely incorporated into PC, by up to 5% in Ordinary Portland Cement (OPC) and up to 15% in Portland Limestone Cement (PLC). The limestone substitution in PC

blends demonstrates desirable compressive strength and durability, by producing carboaluminate that promotes formation of ettringite [4–7]. These chemical conversions have been proven to densify material microstructure, particularly when reacting with additional aluminates in, e.g., metakaolin, which leads to the development of the limestone calcined clay cement (LC³) [8,9]. Concrete based on LC³ has been proven to have equivalent strength and low permeability compared to conventional OPC-based concrete. LC³ also demonstrates global scalability with desirable techno-economic and environmental benefits for field applications [10–12].

Initially introduced in 1990s, Engineering Cementitious Composites (ECC) has been extensively studied as a novel class of ultra-ductile cementitious materials with strain-hardening characteristic [13,14]. Conventional concrete is well known as a brittle material, with less than 0.01% strain capacity under tension. The lack of tensile ductility makes concrete vulnerable to cracking, which could accelerate the ingress of external liquids carrying harmful species and leads to degradation of

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concrete structures, even if the uncracked portion possesses high strength and dense microstructure. ECC is different from conventional concrete, in that it forms multiple fine cracks to attain ultra-high tensile ductility (>2%). Based upon microfiber bridging and micromechanical design framework, crack width in ECC can be autogenously controlled to below 100 μ m, which remarkably retards liquid permeation [15–17]. The self-controlled fine cracks together with the ultra-high composite tensile ductility reduces the need for steel reinforcements and further enhances structural durability and life-cycle performance [18,19].

ECC can be potentially made from LC³-based binders. In general, ECC has a high volume of SCMs, which accounts for more than 50 wt% of binder. This provides flexibility of incorporating calcined clay and limestone in composite formulations with potentially minimal compromise in technical properties. From the durability perspective, the dense microstructure formed by LC³ would be better utilized if crack width can be well controlled. Uncontrolled cracks would otherwise create pathways that facilitate ingress of harmful species, leading to overall structural deteriorations prior to material failure, even the noncracked materials remain intact. As LC³ is inherently brittle, the durability of LC³-based concrete is subjected to uncontrolled cracking and early structural deteriorations in field. Adopting the ECC design framework to develop crack width control for LC³ will substantively enhance structural durability and will mitigate life-cycle impacts on top of the already lowered emissions and energy consumptions at manufacture. Previous studies [20,21] show that blending limestone and calcined clay in ECC binders could result in tensile strain capacities of 0.57-1.58% with PVA fiber and 6.0-8.9% with PP fiber, demonstrating the potential of enhancing LC³ composite tensile ductility through fiber incorporation. The impacts of LC³ on composite crack control, pore structure and matrix chemistry, however, have been left open for discussion.

It is therefore the focus of this study to assess the viability of applying LC³-based binders to the production of ECC with durable chemistry and tight cracks. As the LC³ consisting of 30% metakaolin and 15% limestone has previously demonstrated optimized binding properties [22], this combination is used here to fully replace OPC in typical ECC matrix formulated with high volume fly ash. Limestone of various particle sizes have been adopted in previous studies [23] to tailor the compressive strength of LC³ concrete through the filler effect, which may also pose a potential influence on the ECC ductility and crack width control. As such, two limestone particle sizes are examined for the LC³-based ECC in this study. The composite integration based on the quaternary blends (i. e., PC, metakaolin, limestone and fly ash) are examined from the mechanical and chemical perspectives in which tension, compression and hydrate compositions are characterized. Uniaxial tension experiment, thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) are performed to assist in understanding composite behaviors.

2. Experimental program

2.1. Materials and mix proportion

Chemical compositions of Ordinary Portland cement (Type I, OPC, Lafarge), fly ash (Class F, Headwaters) and metakaolin (Sikacrete, M – 100) used in this study are shown in Table 1. Technical properties of solid ingredients used for ECC matrix are shown in Table 2. All specimens were prepared using F75 silica sand (US Silica), polyvinyl alcohol

(PVA, Kuraray) fibers with physical properties listed in Table 3 and a polycarboxylate-based high-range water-reducing admixture (HRWRA, ADVA198, GCP Applied Technologies) to achieve desirable workability of fresh mixtures. Two different types of limestone (Omya) with median sizes of 3 µm and 12 µm were used. Table 3 lists technical properties of the raw materials used for ECC matrix.

To emulate LC³ composition, 30% metakaolin and 15% limestone were mixed with 55% OPC to form a novel cement. Note that this cement mix is not strictly LC³, due to the absence of additional gypsum source in this experiment. It is therefore used for the purpose of feasibility study. The mix proportions are listed in Table 4 in which three formulations were considered. Conventional ECC with a high fly ash volume was used as reference, i.e., ECC-Ref, whereas two LC³-based ECC mixes (ECC-LC³), i.e., ECC-L3 and ECC-L12, were designed with the two different limestone particle sizes. It should be noted that typical ECC matrix uses a very low water-to-solid (w/s) ratio (i.e., 0.25) compared to that of LC³ mixes typically ranging between 0.35 and 0.5 [24,25]. Mixing was found to be challenging when OPC is directly substituted with LC^3 due to the fine particles and high water demand of calcined clay. With a constant 0.25 w/s ratio, the mixture remained unworkable even the HRWRA was added up to 3.5% by LC³ mass (i.e., 1.1% by binder mass). This dosage approached the upper limit recommended by the HRWRA supplier (i.e., maximum 1.1% and preferably 0.41% by binder mass), and may result in significant delay in setting time. As such, through a set of experimental trials, a higher dosage of HRWRA together with 20% additional mixing water was used for ECC-LC³ mixes to attain the same flowability as that of ECC-Ref. The alternation in w/s ratio would significantly affect mechanical properties as well as microstructure, and may create inconsistencies when comparing ECC-LC³ with ECC-Ref. This is kept in mind during the data interpretation and discussion in following sections.

2.2. Sample preparation

Three batches of ECC specimens were made in accordance with Table 4. Additionally, mortar and cementitious paste samples were prepared for chemical and microstructural analyses. The same mix proportions as that of ECC were followed, except for the removal of PVA fiber for making mortars and the removal of fiber and sand for making cementitious pastes.

The novel ECC followed the same mixing protocol as that of ECC-Ref, which has demonstrated feasibility of field mixing and casting using

Table 2

Technical properties of raw materials used for ECC matrix.

Materials	Grade	Standard	Specific gravity	Particl µm	e size,
				D _{v50}	Range
OPC	Type I	ASTM C150	3.15	15	-
Fly ash	Class F	ASTM C618	2.60	11	-
Metakaolin	Class N pozzolan	ASTM C618	2.60	5	-
Limestone, 3 µm	Purity >96%	-	2.71	3	-
Limestone, 12 µm	Purity >96%	_	2.71	12	-
Silica sand	F-75 quartz	-	2.62	115	53–210

Material	CaO	SiO ₂	Al_2O_3	Fe ₂ O ₃	SO_3	MgO	K ₂ O	TiO ₂	MnO	P_2O_5
OPC Fly ash	67.51 3.40	17.70 52.19	4.17 22.23	3.72 13.49	3.64 2.16	1.96 0.93	0.55 2.56	0.30 1.01	0.13 0.00	0.14 0.11
Metakaolin	0.02	50.83	46.62	0.46	0.14	0.00	0.28	1.65	0.00	0.00

Table 3

Physical properties of PVA fiber.

Length, mm	Diameter, µm	Elongation, %	Density, kg/m ³	Young's modulus, GPa	Tensile strength, MPa
8	39	6	1300	42.8	1600

Table 4

ECC mix proportions.

Mass ratio	ECC-Ref	ECC-LC ³	
		ECC-L3	ECC-L12
Portland cement	1	0.55	0.55
Fly ash	2.2	2.2	2.2
Metakaolin	-	0.3	0.3
Limestone (3 µm)	-	0.15	-
Limestone (12 µm)	-	-	0.15
Silica sand	1.16	1.16	1.16
Water	0.79	0.95	0.95
HRWRA	0.013	0.022	0.022
w/s ratio	0.25	0.30	0.30
PVA fiber, vol%	2	2	2

conventional concrete facilities. Powder ingredients, including PC, fly ash, metakaolin and limestone powder, were mixed with silica sand for 4 min at low speed. Water mixed with HRWRA was then added to the powder ingredients, and was mixed for 6 min to form a homogenous mortar mixture. PVA fibers were slowly added while mixing for 1 min, and were then mixed for another 2 min. The mixture was finalized with an additional 2 min mixing at medium speed. The flow table test prescribed by ASTM C230 was adopted to verify the consistency of ECC fresh properties, and the spread diameter was controlled to 230 \pm 15 mm for ECC-Ref and ECC-LC³. The fresh ECC mixture was cast into two kinds of molds, i.e., dogbone-shaped for uniaxial tension (see Fig. 1) and 50 mm cubic for compression. All ECC specimens were demolded at the age of 24 h, and were then stored in airtight plastic containers to prevent water evaporation. Meanwhile, paste, mortar and additional ECC mixtures were molded into plastic vials and were sealed in airtight bags until the designated testing ages at 3, 7 and 28 days.

2.3. Mechanical and micromechanical characterizations

The hardened ECC-LC^3 were characterized from mechanical and chemical perspectives at different length scales to provide a comprehensive understanding of the composite system. Table 5 lists experimental techniques and the corresponding takeout knowledge.

ECC mechanical properties were examined through compression and tension. Compression test was conducted on 50-mm cubes following ASTM C109. The test was repeated three times with the average

Table 5

Aspect	Experiment	Parameter
Mechanical	Compression Uniaxial tension	Compressive strength σ-ε relationship First-cracking strength Ultimate tensile strength Tensile strain capacity
Chemical	Single-crack TGA XRD MIP	σ-δ relationship Hydration process Mineral alteration Pore structure

reported. For the tension test, dogbone-shaped specimens were loaded at a rate of 0.5 mm/min on an Instron loading frame. Two linear variable differential transformers (LVDT) were mounted to the specimens to capture extensions of the 80-mm middle section shown in Fig. 1. Four repetitions were conducted.

After attaining the ultimate tensile stress, ECC specimens were unloaded for crack measurements. An optical microscope (Infinity, X–C21) with a resolution of 10 μ m was used. Crack numbers and widths were measured on the centerline along the longitudinal direction within the 80-mm section. Note that cracks measured in this manner are essentially residual cracks due to the unloaded state, and the total crack widths would not equate to the ultimate tensile deformation shown on σ - ϵ curves. The distribution of residual crack width is not representative of realistic cracks under field conditions in which materials are normally loaded and cracks are kept in tension. Nevertheless, residual crack widths were used in this study as a comparison of crack width control capability between ECC-LC³ and ECC-Ref.

To obtain tensile σ - δ relationships, single-crack experiment was conducted using dogbone-shaped specimens. To generate a concentrated crack under tension, ECC specimens were pre-notched in the middle, as graphically illustrated in Fig. 2. The loading process was programmed in the same protocol as that of the uniaxial tension tests. Three repetitions were conducted.

2.4. Chemical, mineralogical and microstructural characterizations

Typical ECC formulations are based on high-volume fly ash binary system, although ternary and even quaternary systems have been previously applied to ECC [26]. LC^3 itself is a ternary binder. Its compatibility with the high-volume fly ash system in ECC needs to be validated. At 3, 7 and 28 days, cementitious pastes and mortars were crushed into chunks smaller than 5 mm, and ECC cast in vials were saw-cut into 5-mm thin sections. All samples were dried using solvent exchange by fully immersion in isopropanol for 7 days after which the solvent was removed in a vacuum desiccator. The dried solid samples were used for pore structure analysis, whereas remaining samples were manually



Fig. 1. Dimensions of dogbone-shaped ECC specimen for uniaxial tension test.



Fig. 2. Simplified drawing illustrating dimensions (left) and location (right) of pre-notch on cross section of dogbone-shaped specimens for single-crack measurement.

grinded using a ceramic pestle and passed a 75 μ m sieve for TGA. Moreover, paste samples were further ground into powders smaller than 25 μ m for XRD. To assist in comparing relative intensities of various mineralogical phases, 10 wt% lithium fluoride was thoroughly mixed with the fine powders as an internal reference. Rietveld refinement, however, was not performed on the obtained diffraction patterns due to the significant amorphous intensities induced by the ultra-high volumes of fly ash and metakaolin.

TGA was conducted on cement paste, mortar and ECC. A TA Instruments (Model: SDT650) Simultaneous DSC/TGA equipment was employed. About 10 mg of powder samples was mounted to an alumina crucible, which was heated from room temperature up to 1100 °C at a ramping rate of 10 °C/min. The mass of the crucible and sample was continuously recorded during the heating process in which the furnace was purged with pure N2 gas at a flow rate of 50 mL/min. For mineralogical analysis, a Rigaku SmartLab high resolution XRD was used. The 25 µm powder samples were front loaded and the top surface was lightly smoothed using a glass spatula. The source of the X-rays were generated through the Cu-Ka radiation, with diffraction patterns collected in the range of $5-50^{\circ}$ 20 at 0.02° per step. Mineral phases were identified using MDI Jade 2010 and were cross-checked with HighScore Plus. To understand how the LC^3 chemistry and fiber bridging would affect the physical pore structure, MIP was conducted on pastes, mortars and ECC at 28 days. A Micromeritics AutoPore V Mercury Porosimeter was used, and the contact angle of mercury was assumed at 130° for all samples. Mercury was intruded into the samples from atmospheric pressure up to 420 MPa, which corresponded to a minimum pore diameter of about 3 nm.

3. Results and discussion

3.1. Compressive strength

As a common metric of concrete quality, compressive strength was measured on ECC cubes. Fig. 3 shows evolution of compressive strength from 3 days to 28 days. At 3 days, the ECC-LC³ attained 14.2 MPa and 15.6 MPa for ECC-L3 and ECC-L12, respectively, whereas ECC-Ref achieved 22.3 MPa. Compressive strengths of ECC-LC³ were found to continue increasing after 3 days and were nearly doubled at 7 days,



Fig. 3. Evolution of ECC compressive strength from 3 days to 28 days.

when strength gains of ECC-LC³ began to slow down, achieving 32.1 MPa for ECC-L3 and 31.3 MPa for ECC-L12 at 28 days. Their counterpart, ECC-Ref, exhibited a continued gain of compressive strength over the period of 3-28 days and attained a 28-day strength of 55.3 MPa. This strength gain can be attributed to the clinker hydration and the relatively slower fly ash pozzolanic reaction, which would take over 90 days to form strength comparable to that of fly ash-free samples [24]. Compared to ECC-Ref, the lower compressive strengths of ECC-L3 and ECC-L12 at 28 days are ascribed to the 20% higher w/s ratio needed for attaining adequate workability and fiber dispersion. Additionally, the hydration of LC³ produces less calcium hydroxide due to the lower clinker content, which retards the fly ash pozzolanic reaction in the ECC-LC³ binder. The coupled use of LC³ and high-volume fly ash in this study essentially creates a chemical competition between metakaolin and fly ash for the limited quantity of calcium hydroxide and therefore lowers the 28-day compressive strength for ECC-LC³ compared to ECC-Ref.

The impact of limestone fineness on the ECC-LC³ compressive strength appears to be insignificant in the D_{v50} range of 3–12 µm. Fig. 3 suggests that the ECC-L3 made with a limestone D_{v50} of 3 µm exhibited slightly lower compressive strengths at 3–7 days but a relatively higher 28-day compressive strength compared to the ECC-L12. This trend seems to be contradictory to the previous finding [23] that a finer limestone could enhance cement hydration and strength gain of LC³ mortars. Nevertheless, the aforementioned discrepancy of compressive strengths

between ECC-L3 and ECC-L12 in Fig. 3 is not statistically significant at a 95% confidence level, indicating that the influence of limestone fineness ($D_{v50} = 3-12 \ \mu m$) on the composite compressive strength is marginal with respect to the variability related to fiber incorporation. Further investigations covering a broader range of limestone fineness are needed for clarification.

3.2. Uniaxial tensile behaviors

3.2.1. σ - ε relationship

The composite tensile properties were examined through uniaxial tension of the dogbone-shaped specimens. Fig. 4 presents the stressstrain relation from which key tensile parameters are summarized in Fig. 5. The ECC-LC³ displayed distinct strain-hardening patterns with ultimate tensile strains over 3% at all ages. As shown in Fig. 5a and b, at 3 days, replacing OPC with LC³ was found to create higher first-cracking and ultimate strengths. Specifically, the ECC-L3 mix led to 14% and 18% increases in first-cracking and ultimate strengths over those of ECC-Ref, respectively. It is interesting that limestone particle size poses a trivial effect on tensile strength development, although fine limestone particles are known to expedite hydration as nucleation seeds. Tensile strengths of ECC-Ref began to exceed that of ECC-LC³ at 7 days, and attained a first-cracking strength of 4.0 MPa and an ultimate strength of 6.5 MPa at 28 days. In contrast, ECC-LC³ showed first-cracking strengths of ~2.5 MPa and ultimate strengths of tensile strengths of ~2.1 means of ~2.1



Fig. 4. ECC tensile stress-strain relationships: (a) ECC-Ref, (b) ECC-L3, and (c) ECC-L12.



Fig. 5. ECC tensile properties: (a) first-cracking strength, (b) ultimate strength, and (c) strain capacity.

strengths between ECC-LC³ and ECC-Ref were consistent with the results of compressive strengths, suggesting that the LC^3 -based ECC developed in this study had a lower matrix mechanical integrity compared to conventional ECC.

ECC-LC³ exhibited clearly higher strain capacities than ECC-Ref. As shown in Fig. 5c, at 28 days, the ECC-L3 and ECC-L12 attained strain capacities of 6.5% and 5.2%, respectively, whereas the strain capacity of ECC-Ref was approximately 4.2%. The strain capacities of ECC-LC³ were over 500–600 times that of conventional concrete. This high tensile ductility indicates a significant enhancement of energy absorption capacity and material durability, which are particularly useful for seismic design and structural applications in harsh environments. Previous lifecycle analysis (LCA) of ECC overlays suggested a minimum 50% reduction in life-cycle emissions and cost, essentially due to an assumed 2% tensile strain capacity [18]. Therefore, the high tensile ductility of the newly developed LC³-based ECC is anticipated to significantly mitigate life-cycle impact, which deserves further investigations with particular regard to durability.

The influence of limestone fineness was found to be insignificant on the ECC first-cracking strength and ultimate strength at 3–28 days, as well as on the ECC strain capacity at 3–7 days. At 28 days, however, a higher strain capacity was observed for ECC-L3 than ECC-L12, indicating that decreasing the limestone particle size may enhance composite tensile ductility in the long term.

3.2.2. Residual crack width distribution

Apart from tensile ductility, crack width control is critical to material and structural durability. Unlike the conventional brittle concrete, ECC possesses a unique capability of controlling crack width in an autogenous manner [13]. The distributions of residual crack width is presented at an interval of 20 μ m in Fig. 6. These crack patterns were obtained after the release of tension, and would differ from realistic field conditions in which cracked specimens are normally loaded. As shown in Fig. 6, ECC-Ref exhibited 49 cracks and the average crack width was 22 μ m. The ECC-LC³ formed less cracks with relatively larger crack widths at an average of 44–71 μ m. The relatively large crack width can be associated with the higher w/s ratio for the LC³ system, which increases the matrix porosity and lowers the contact area between the fiber and matrix. Consequently, a lowered fiber/matrix interfacial frictional bond may result for ECC-LC³, promoting the fiber slippage and crack opening under tension.

Compared to ECC-L3, ECC-L12 with a larger limestone particle size exhibited a more saturated multiple cracking pattern at a tighter average residual crack width as shown in Fig. 6c. The increased crack number indicated that the ECC-L12 matrix appeared to be more vulnerable to crack initialization, which may relate to a less dense matrix when a coarser limestone was incorporated. As the crack number and width shown in Fig. 6 were measured after attaining the maximum tensile strain, the relatively high strain capacity of ECC-L3 may also contribute to the larger residual crack width, making the crack control ability



Fig. 6. Residual crack width distribution: (a) ECC-Ref, (b) ECC-L3, and (c) ECC-L12.

incomparable between ECC-L3 and ECC-L12. Therefore, further investigations through in-situ crack width measurement under tension, such as digital image correlation [27], would be useful for clarifying the intrinsic crack width distributions at different limestone fineness.

3.2.3. σ - δ relationship

The σ - δ relationships of ECC-L3 and ECC-L12 displayed similar patterns, which were clearly different from that of ECC-Ref. Fig. 7 shows the experimental data obtained at 28 days. It was found that ECC-Ref possessed a higher crack bridging capability σ_0 than did the ECC-LC³. This is due to the denser interfacial transition zone between fiber and the reference matrix, which is consistent with the porosity measurements discussed in Section 3.4. Correspondingly, the lower matrix strength of ECC-LC³ (primarily led by the 20% higher w/s ratio) reduces the stress needed for initiating new multiple cracks, and therefore is able to meet the stress criteria that favors the formation of composite strainhardening properties [14]. From the energy perspective, both ECC-LC³ and ECC-Ref showed higher complementary energy Jb' with respect to their matrix fracture toughness J_{tip} , which confirms the high tensile ductility and strain-hardening characteristics. The σ - δ relationship appeared to be close between ECC-L3 and ECC-L12, suggesting that the influence of limestone particle size was insignificant compared to the single-crack measurement variability. The composite strain-hardening properties can be further associated with fiber failure type at the fractured cross-section. Fig. 8 shows SEM images of fiber ends taken in ECC-LC³, where pulled out (Fig. 8a) and ruptured fiber ends (Fig. 8b) were both identified. There was a likely trend in ECC-LC³ that the pulled out fiber end appeared comparatively more common in the observation. This is similar to the fiber failure type of ECC-Ref and verifies the strain-hardening properties of LC³-based ECC.

3.3. TGA analysis

To access the chemical evolutions in the matrix materials, TGA and XRD were conducted on the cementitious pastes. Fig. 9 shows TGA mass loss and corresponding DTG curves from 3 days to 28 days, while the mass loss associated with dehydrations of calcium hydroxide (CH) and other hydrate-bound water are compared in Fig. 10. It was found that the LC³ mixes likely hydrated faster at early ages relative to the conventional ECC matrix. For example, at 3 days as shown in Fig. 10b, the hydrate-bound water contents were 3.8% and 3.6% (by ignited mass) for ECC-L3 and ECC-L12 binders, respectively, whereas that for the ECC-Ref binder was 3.4%. This difference between ECC-L3 and ECC-Ref binders appeared more prominent at 7 days, when the bound water content achieved 5.1% for ECC-L3 but only 4.4% for the latter. This trend, however, was reversed after 28 days, forming the highest bound water content for the ECC-Ref binder at 28 days. In ECC binders, Portland cement clinker is the primary contributor to the uptake of bound water through hydration. Pozzolanic reactions of fly ash and metakaolin take up additional water besides the consumption of CH. As such, the



Fig. 7. Tensile $\sigma\text{-}\delta$ relationships at 28 days: (a) ECC-Ref, (b) ECC-L3, and (c) ECC-L12.



Fig. 8. Observation of PVA fibers at fractured surface of ECC-LC³ after uniaxial tension: (a) pulled out end, and (b) ruptured end.

relatively high usage of Portland cement in ECC-Ref is accountable for the high bound water content at 28 days by promoting the hydratebound water directly and increasing CH for pozzolanic reactions. The relatively more rapid hydration of ECC-LC³ before 7 days can be associated with the high w/s ratio and the presence of fine metakaolin, which tends to manifest at an early age of cement hydration.

Another take away from the DTG curves is associated with the dehydroxylation stage. As shown in Fig. 9d-f, the CH peak intensities

were found substantially lower in LC^3 binders regardless of curing age. The CH content shown in Fig. 10a was kept at ~0.6% at all ages, whereas the ECC-Ref showed a CH content consistently over 1.2%, with an uptick from 3 days to 7 days followed by a decrease to 28 days. The cause of the low CH intensities in LC^3 binders can be attributed to the low clinker content, as well as an increased consumption led by pozzolanic reactions competing between metakaolin and fly ash.

The ECC-L3 and ECC-L12 binders exhibited comparable TGA/DTG



Fig. 9. TGA mass loss and DTG curves of cementitious pastes.



Fig. 10. Evolution of (a) CH and (b) bound water contents in ECC binders.

profiles, except for the relatively high bound water contents observed for the former at 3–7 days. It was indicated that cement hydration tended to be accelerated in ECC-L3 due to the fine limestone particle size that promotes the hydrate precipitation at early ages. This impact, however, was not reflected in the results of ECC compressive and tensile strengths in Sections 3.1-3.2. The comparison between ECC-L3 and ECC-L12 suggested that the impact of limestone fineness on early-age material mechanical integrity becomes marginal on the composite level and is potentially overshadowed by variabilities relevant to fiber

incorporation.

3.4. XRD analysis

The XRD results confirm that substituting OPC with LC^3 in the ECC matrix lessens the CH intensities. As suggested in Fig. 11, it was clear that CH was nearly depleted at all ages in the LC^3 binders. By contrast, the ECC-Ref samples exhibited consistent peaks of CH as identified at 18.1° and 36.6° 20. Low CH contents may reduce material resistance to



Fig. 11. XRD patterns of cementitious pastes (Ettr: ettringite, CH: portlandite, CS: calcium silicates, C: calcite). 10% LiF was added as an internal reference.

carbonation and potentially result in an increasing risk of rebar corrosion in reinforced applications. This was recognized in previous studies on the development of LC^3 -based mortar/concrete [28] and might become aggravated when additional SCMs are incorporated, e.g., fly ash in ECC. The high tensile ductility and crack width control ability of ECC may help overcome this inherent deficiency of blended cement by reducing the need for steel reinforcement and slowing down the rate of corrosion.

Apart from CH, additional crystalline components in the LC^3 -fly ash pastes comprised calcite and ettringite at 3–28 days. In LC^3 binders, the incorporation of natural limestone was responsible for the presence of calcite, which showed comparable intensities between ECC-L3 and ECC-



Fig. 12. Pore size distributions of cementitious pastes, mortars and ECC at 28 days.

L12 but became less visible in ECC-Ref. The ettringite peaks, however, appeared to be of close intensities irrespective of the binder composition or curing age. All the ettringite peaks displayed substantially weak intensities in contrast to the LiF reference (added at 10% by sample mass), potentially due to the ultrahigh dosage of fly ash (69% by binder mass) that dilutes cement hydration products. The promoting effect on ettringite precipitation led by the reaction between limestone and monosulfoaluminate appeared to be less prominent in the XRD results and was a potential consequence of the relatively low ettringite contents in the binder composition.

3.5. Pore structure

Table 6

Pore structure analysis suggests that the dispersed fibers do not significantly affect interconnectivity of pores in LC³ matrix, and the use of LC³ binder could potentially refine ECC pore structure through redesign of matrix formulation. The MIP pore size distributions are shown in Fig. 12, with total porosity and pore size listed in Table 6. It was found that the LC³-based ECC showed a relatively coarser pore structure compared to the conventional ECC. For example, the total porosity was measured 26.0% for ECC-L3 and 27.6% for ECC-L12, but was only 19.9% for ECC-Ref. The same trend was found on the critical pore diameter, which was 41 nm for ECC-L3 and ECC-L12, and was only 12 nm for ECC-Ref. Critical pore diameter represents the size of most common pores in a porous sample and a high critical pore diameter is often associated with easier access to the permeation of external liquids. A previous study conducted by Avet and Scrivener [29] on LC³ pastes with a w/s ratio of 0.4 identified that a limiting critical pore radius of 3-5 nm would be posed on clinker hydration and pore structure refinement after 3 days if the calcined kaolinite content of clay was higher than 65%. This limiting pore radius, however, is not reached in the LC³-fly ash blends used here for ECC, even up to 28 days with a lower w/s ratio (0.3). This indicates that blending fly ash with LC^3 is a viable approach for producing ECC, in addition to reported merits to workability, mechanical properties and CO₂ emissions [25].

The incorporation of PVA fiber did not cause substantial changes in the pore structure regardless of the matrix material used. As shown in Fig. 12, the difference of total intruded volume between mortar (Fig. 12b) and ECC (Fig. 12c) was found minimal for LC³ and reference mixes. This is also confirmed by the porosity results in which all ECC samples showed porosities of $\pm 1\%$ difference from their mortar counterparts as seen in Table 6. The fiber inclusion did not significantly affect the sample density as identified by MIP. In fact, the experimental variation seemed to overwhelm the impact of fiber inclusion on pore structure, as porosity, bulk density and apparent density appeared comparable between ECC and mortar samples. This seems inconsistent with a previous study [30], which reported that incorporating 2 vol% PVA fiber could lead to more than 3% increase in porosity of pores larger than 300 nm. As PVA fibers contribute marginal pore volume due to their low usage in ECC, the increase in ECC porosity could be largely attributed to inadequate fiber dispersion that creates air cavities in vicinity of fiber surface. However, the MIP findings in this study suggest that the increase in porosity led by fiber incorporation could be minimized if proper fiber mixing and dispersion could be achieved.

The total porosities of ECC samples were further broken down as a

function of pore diameter to assist in understanding their impact on material performance. Four ranges of pore diameter are considered in conjunction with physical properties in the context of cement-based materials, as shown in Fig. 13, including void (>100 nm), large capillary pore (50-100 nm), medium capillary pore (10-50 nm) and small capillary pore (<10 nm) [31]. All three ECC samples displayed structures dominated by the medium capillary pore, which accounts for 47%, 48% and 42% of total porosities in ECC-L3, ECC-L12 and ECC-Ref, respectively. The ECC-Ref showed the highest volume fraction of small capillary pore, i.e., 31%, versus 18–19% identified in ECC-LC³. This is attributed to the lower w/s ratio and higher clinker content in ECC-Ref. It was interesting that the use of LC³ in place of OPC was found to decrease the volume fraction of void, even after increasing w/s ratio by 20%. As shown in Fig. 13, about 22% of pores in ECC-Ref were found to be void, whereas in ECC-L3 and ECC-L12, the volume fractions of void were lowered to 15%. Correspondingly, the volume fraction of large capillary pore increased from 5% to 19% as a result of LC³ substitution for OPC. Given the comparable average pore diameters between ECC-LC³ and ECC-Ref and the lowered fraction of voids by LC³ even at a 20% higher w/s ratio, it is plausible to further refine the pore structure of ECC-LC³ by tailoring binder compositions to reduce the water demand while maintaining sufficient workability.

3.6. Environmental and economic impacts

The environmental and economic assessments of ECC-LC³ suggest that using LC³ in place of OPC for producing ECC lowers the overall energy and CO₂ footprints while marginally reducing the manufacturing cost. Table 7 lists the material sustainability indicators (MSIs) of the main ingredients used for producing ECC, including energy consumption, CO₂ emission and cost. The MSIs capture material manufacturing phase at a cradle-to-gate basis and are able to reflect the composite sustainability performance. By combining mix proportions, the impacts of each ECC mix are listed in Table 8 with respect to traditional OPCbased concrete. The production of traditional ECC mix, i.e., ECC-Ref, possesses obviously higher energy consumption, CO2 emission and manufacturing cost compared to traditional concrete. This is mainly attributed to the use of high performance polymeric fibers, which accounts for nearly 50% of energy consumption and cost of the overall composite material. By switching to LC³ binder, the composite embodied energy and CO₂ emission are found to decrease by 8.5% and 31.5%, respectively. The composite CO_2 emission of ECC-LC³ is indeed even lower for the ECC-LC³ (267 kg/t) than for the traditional concrete (373 kg/t). From the economic point of view, comparable costs were found for ECC-LC³ and ECC-Ref, both of which are more than three times that of traditional concrete.

The overall composite performance are compared between ECC-LC³ and ECC-Ref as given in Fig. 14, in terms of technical properties, i.e., compressive strength, tensile ductility and residual crack width, environmental impacts, i.e., energy consumption and CO_2 emission, and manufacturing cost. All indices are regulated to their values obtained on ECC-Ref, which are set as a single unit. Prominent differences between ECC-LC³ and ECC-Ref include higher tensile ductility, wider crack width, lower compressive strength and lower CO_2 emission after switching from OPC to LC³. Note that although crack width of ECC-LC³

Porosity, pore size and density at 28 days.									
Sample	Paste			Mortar			ECC		
	L3	L12	Ref	L3	L12	Ref	L3	L12	Ref
Porosity, %	35.5	33.7	27.5	26.7	27.0	19.1	26.0	27.6	19.9
Critical pore diameter, nm	32	32	20	41	32	16	41	41	12
Average pore diameter, nm	16	15	12	15	15	12	17	17	12
Bulk density, g/cc	1.56	1.67	1.76	1.77	1.76	1.95	1.75	1.79	1.96
Apparent density, g/cc	2.42	2.51	2.43	2.42	2.42	2.41	2.36	2.47	2.45



Fig. 13. Pore volume fraction in ECC samples at 28 days.

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Energy consumption, $\rm CO_2$ emission and cost of ingredients for ECC production.

Component	Energy, GJ/t	$\rm CO_2$ emission, kg/t	Cost, USD/t
OPC [11]	4.72	820	72.02
LC ³ [11]	3.99	550	56.41
Fly ash ^a	0	0	26.5
Silica sand	0.226 [32]	33 [<mark>33</mark>]	25 ^b
Superplasticizer [34]	35	1667	1211
PVA fiber [35,36]	101	1710	12,670

Note:a: fly ash is considered as a byproduct from coal industry; b: cost is based on market price of construction sand.

Table 8

Environmental and economic impacts of ECC made with LC³.

Material	Energy, GJ/t	CO ₂ emission, kg/t	Cost, USD/t
Traditional concrete	2.5	373	108
ECC-Ref	4.7	390	398
ECC-LC ³	4.3	267	387

doubled that of ECC-Ref, ECC-L12 still shows tight cracks with an average width of 44 $\mu m.$ This is adequately tight to slow down ingress of external liquids that carry harmful species [15,17] and to provide favorable conditions for developing self-healing ability [37,38]. The lower compressive strength of ECC-LC³ is largely caused by the high w/s ratio and high siliceous fly ash content, and is a potential challenge for its field use. As the w/s ratio designed in this study is mainly governed by requirements of matrix workability and fiber dispersion, lowering siliceous fly ash content or adjusting mixing protocol is likely a solution. Additionally, ECC-LC³ shows clearly high tensile ductility compared to ECC-Ref and traditional concrete. This characteristic, together with the relatively lower compressive strength, makes ECC-LC³ suitable for repair application and seismic design. From the environmental point of view, ECC-LC³ shows good promise in reducing CO_2 emission, due to the reduced need for limestone calcination for clinker production. The composite embodied energy is slightly reduced when switching from OPC to LC³, since the saved energy tends to be compromised by the use of high-energy intensity PVA fiber. Likewise, the manufacturing cost of ECC-LC³ appears comparable to that of ECC-Ref, because of the high unitary cost of PVA fiber even with modest usage (2 vol%). To that end, it is critical to seek alternative fibers for further advancing sustainable development and broader field adoptions of ECC-LC³.



Fig. 14. Technical, environmental and economic comparison between ECC-Ref and ECC-LC³.

4. Conclusions

This study demonstrates a novel adoption of limestone calcined clay cement (LC^3) for developing Engineered Cementitious Composites (ECC) with high tensile ductility and strain hardening characteristics. The LC^3 -based ECC shows a tensile strain capacity of up to 6% and an average residual crack width below 50 µm. The 28 days composite compressive strength of 32 MPa is lowered due to the use of a higher water content. Using different particle sizes of limestone powder does not significantly affect composite compressive or tensile strength, but is found to alter tensile ductility and residual crack width. Between the median particle diameters of 3–12 µm, a finer limestone increases the composite tensile ductility but produces a less saturated multiple cracking pattern on the specimen surface. Additionally, the lowered compressive and tensile strengths of LC^3 -based ECC could be potentially enhanced through redesign of matrix formulation to meet specific needs for different load conditions.

Apart from micromechanical reinforcements, the inclusion of short random polymeric fibers in LC^3 -based ECC shows little impacts on matrix chemistry or pore structure. At a 2% fiber volume, porosity and pore size appear comparable between matrix materials and composites. The use of LC^3 lowers the volume fraction of pores larger than 100 nm in diameter, despite a higher w/s ratio used in LC^3 -based ECC compared to that used in OPC-based ECC. Using LC^3 shows a potential trend of refining ECC pore structure and densifying composite microstructure if equivalent water content can be achieved.

From the environmental point of view, using LC^3 in ECC shows a drastic low carbon potential by embodying 28% less CO_2 emissions compared to the manufacture of traditional concrete, but only a slightly reduction in energy consumption and production cost. The reduction in carbon intensity, together with the enhanced durability led by autogenously tight crack width and high tensile ductility, enhance the sustainability of LC^3 -based materials and infrastructures.

Declaration of competing interest

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

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