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Durability Properties of High Performance Fiber Reinforced Cementitious Composites Incorporating High Volumes of Fly Ash

Mustafa Sahmaran[b], *Mustafa Tokyay*[a]

[a] *Department of Civil Engineering, Gaziantep University, Gaziantep, Turkey, e-mail: sahmaran@gantep.edu.tr*

[b] *Department of Civil Engineering, Middle East Technical University, Ankara, Turkey, e-mail: mtokyay@metu.edu.tr*

Abstract

This paper discusses the influence of the high volumes of fly ash on the fire and frost resistance and microstructure of the Engineered Cementitious Composites (ECC). Composites containing two different contents of fly ash as a replacement of cement (55 and 70% by weight of total cementitious materials) are examined. For frost resistance, mixtures are exposed to the freeze and thaw cycles up to 300 cycles in accordance with ASTM C666, Procedure A. For fire resistance, mixtures are exposed to the temperatures up to 800 ^{o}C for one hour. Fire and frost resistance of the mixtures are determined in terms of the residual ultrasonic pulse velocity and mass loss. The air-void characteristics of mixtures are also studied using linear transverse method. The role of fly ash is discussed through the analysis of microstructure. The microstructural characterization is examined before and after exposure to frost and fire deterioration by using scanning electron microscopy. Results indicate that frost resistance of ECC mixtures containing no entrained air is worsened, but fire resistance of ECC mixtures is improved with the addition of fly ash.

Keywords: Engineered Cementitious Composites (ECC); Durability; Fly Ash.

1. Introduction

In recent years, the effort to modify the brittle nature of ordinary concrete has resulted in modern concepts of ultra-high performance fiber reinforced cementitious composites (UHP-FRCC), which are characterized by tensile strain-hardening after first cracking. Depending on its composition, its tensile strain capacity can be up to several hundred times that of normal and fiber reinforced concrete. Engineered Cementitious Composites (ECC) is a special type

of UHP-FRCC designed based on micromechanical principles to strain harden in tension. It allows optimization of the composite for high performance represented by extreme ductility while minimizing the amount of reinforcing fibers, typically less than 2% by volume [1-3]. Unlike other concrete materials, ECC strain-hardens after first cracking, similar to a ductile metal, and demonstrates a strain capacity up to 500 times greater than normal concrete. Tensile strain capacities of 2 to 5% have been produced easily in the field with materials and equipment normally used in the concrete industry. Along with tensile ductility, the unique crack development within ECC is critical to its durability. Different from ordinary concrete and most fiber reinforced concretes, ECC also exhibits self-controlled crack widths under increasing load. Even at large imposed deformation, crack widths of ECC remain small, less than 100 μm.

Mineral admixtures such as fly ash (FA), silica fume and ground granulated blast furnace slag improve the engineering properties of concrete when they are used as a mineral additive or partial replacement of cement. Among these mineral admixtures, FA is a finely divided residue of the very fine ash that is a by-product from the combustion of powdered coal in power plants. A recent development in the production of ECC industry has been to use FA as partial replacements for Portland cement in the production of ECC. The addition of FA to ECC alters the microstructure of the composites. The changes in microstructure improve robustness of tensile ductility while retaining a long-term tensile strain of approximately 3% [4-6], but their effect on the durability of the composite is not fully known. Moreover, with an increase of the FA amount, the crack width is reduced from about 100 μm level to 10-50 μm level or sometimes even lower than 10 μm level, which may benefit the long term durability of high volume fly ash (HVFA) ECC structures.

With the current extensive and high volume use of FA in ECC, a thorough understanding of the impact of fire and frost on HVFA-ECC is urgently needed, particularly in light of the rise in fire and frost deterioration in normal concrete structures in recent years,. This study was undertaken to obtain more information on the frost and fire resistance of ECC, particularly on the influence of FA. ECC mixtures with two different FA to Portland cement (FA/C) ratios (1.2 and 2.2) were prepared. The air-void characteristics of mixtures were studied using linear transverse method. The role of FA was analyzed in terms of microstructure and fiber–

matrix interactions as a function of heat treatment and frost exposure by using microscopy analysis.

2. Experimental Studies

2.1 Materials, Mixture proportions and Basic Mechanical Properties

ECC mixtures with FA/C ratio of 1.2 and 2.2 by weight (55 and 70% by weight of total cementitious materials) were used in this investigation, details of which are given in Table 1. Type I ordinary Portland cement (C), silica sand with an maximum size of 400 μm, Class-F fly ash (FA) conforming to ASTMC 618 requirements, polyvinyl alcohol (PVA) fibers, and a polycarboxylate based superplasticizer (SP) were used. The chemical compositions and physical properties of the cement and FA are reported in Table 2. The PVA fibers had an average diameter of 39 μm, average length of 12 mm, a tensile strength of 1600 MPa, a density of 1300 kg/m^3, an elastic modulus of 42.8 GPa, and a maximum elongation of 6.0%.

Table 1. Mixture properties of ECC

Mix ID.	Ingredients, kg/m^3						FA/C	Compressive Strength, MPa	
	C	FA	Water	PVA	Sand	SP		14-d.	28-d.
ECC1	558	669	326	26	446	2.3	1.2	39.2	62.5
ECC2	375	823	318	26	435	2.0	2.2	27.7	54.1

Table 2. Properties of cement and fly ash

	Chemical Composition, %									Physical Properties		
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	LOI	Spec. Grav.	Ret. on 45 μm, %	Water Req., %
C	61.8	19.4	5.3	2.3	0.95	3.8	1.1	0.2	2.1	3.15	12.9	-
FA	5.57	59.5	22.2	3.9	-	0.2	1.11	2.75	0.2	2.18	9.6	93.4

Table 1 shows compressive strength test results of the ECC mixtures cured in an environmental chamber at a temperature of 23 ± 2°C and a relative humidity of 95 ± 5% until the age of testing. The compressive strength was computed as an average of three 50 mm cubic specimens. As seen from Table 1, the compressive strength of ECC decreased with increasing FA content. However even at almost 70% replacement of Portland cement with FA (FA/C = 2.2), the compressive strength of ECC at 28 days can be more than 50 MPa.

2.2 Specimen Preparation and Testing

Frost resistance and air-void characterization

From each mixture, eight 400×100×75 mm prisms were prepared for the freezing and thawing test and determination of air-void characteristics. All specimens were cast in one layer without compaction, demolded at the age of 24 hours, and moist cured at 23±2 ^{o}C for 13 days. For frost resistance, mixtures are exposed to the freeze and thaw cycles up to 300 cycles in accordance with ASTM C666, Procedure-A [7]. The air-void content and spacing factor of hardened ECC and ECC matrix (without fiber) mixtures were also determined by modified point count method according to ASTM C457 [8].

Fire resistance and microstructure characterization

Several 50 mm ECC cubes were cast to determine residual physical and microstructural properties. Specimens were demolded 24-hour after casting, and conditioned in an environmental chamber at a temperature of 23±2 ^{o}C and a relative humidity of 95±5% until the age of 28 days. The specimens were heated to targeted temperatures at the age of 28 days, and their residual properties were then investigated. The heating equipment used in the investigation was a computer-controlled, electrically heated furnace. In the furnace, cubes were heated at a constant rate of about 15 ^{o}C/min to reach the prescribed temperatures. Four maximum temperatures (200, 400, 600 and 800 ^{o}C) were chosen. When the targeted peak temperature was reached, the furnace temperature was maintained constant for 60 minutes. After that, the samples were allowed to cool naturally to room temperature.

In this study, Scanning Electron Microscope (SEM) observation was used to identify the changes occurring in the microstructure of hardened ECC control (unheated) specimens and specimens subjected to various elevated temperatures. The results of the microscopic investigations gave a good explanation of the change in macro behavior of ECC. The weight of each specimen was also measured before and after exposure in order to calculate the mass loss of fire-deteriorated specimens.

3. Experimental Results and Discussions

3.1 Frost Durability

3.1.1 Air-void characterization

Air-void parameters of the hardened ECC mixtures, determined by modified point count method according to ASTM C457, are shown in Table 3, along with the air content measured in the fresh state according to ASTM C231. For each mixture, only the average values obtained from two specimens are shown in the table. As seen in Table 3, although no air entraining admixture was added to the ECC mixtures, the air contents of these mixtures in the fresh state, as measured by ASTM C231, gave values between 6 to 7%, and in the hardened state, as measured by ASTM C457, gave values of more than 7% for all mixtures. These amounts of air content seemed to be adequate for freeze-thaw durability [9]. The apparently high air content in these mixtures may have resulted from the presence of PVA fiber, absence of coarse aggregate and the higher viscosity of the ECC matrix during the fresh state [10]; the PVA fiber, fine particles and high viscosity tend to prevent some of the air bubbles from rising to the surface during placing operations.

Table 3. Air-void parameters of ECC mixtures

	ECC1 (M45)	**ECC2**
Fresh air content (%)	7.3	7.1
Hardened air content (%)	8.2	8.9
Specific surface (mm^{-1})*	25.6	39.5
Spacing factor (mm)*	0.241	0.149
Average chord length (mm)	0.156	0.101

**: For freeze/thaw resistant concrete, the American Concrete Institute (ACI) recommends that [9]: Min. specific surface = 24 mm^{-1}, and Maximum spacing factor = 0.2 mm.*

Hardened air content of 8.2 and 8.9%, spacing factors of 0.241 and 0.149 mm and specific surfaces of 25.6 and 39.5 mm^2/mm^3 were determined for ECC1 and ECC2 mixtures, respectively. Though the spacing factor values of ECC1 (0.241 mm) slightly exceed the generally accepted value of 0.200 mm for good freeze-thaw durability, this lack of an apparently ideal air-void system has not adversely affected the frost durability of ECC1, as indicated in the following section. From the table, it can be observed that the increase in the

FA content in hardened ECC mixtures leads to a significant decrease in spacing factor. An almost similar air content together with a lower spacing factor implies that the average bubble size is decreased with the increase in the FA content. This is likely due to the fact that an increase in FA content results in an increase in volume of paste due to its lower density and pore refinement of FA.

3.1.2 Freezing and thawing resistance

The addition of FA on frost durability of ECC mixtures was assessed by the computation of mass loss, which is a measure of scaling. To measure the internal damage caused by freezing and thawing cycles, the changes in pulse velocity through a prism were also measured. The freeze-thaw durability test results are summarized in Table 4. Table 4 demonstrates that, both ECC mixtures showed excellent performance when exposed to freezing and thawing cycles, even after 300 cycles. A maximum of 1.3% and 2.2%, and 8.0% and 4.7% mass and pulse velocity losses, respectively, were measured for the ECC1 and ECC2 specimens, respectively. Note that at the end of 300 cycles, ECC2 has a higher relative pulse velocity change and mass loss values than ECC1 at the same number of freeze-thaw cycles although ECC2 had a higher hardened air content and significantly lower spacing factor than ECC1. Therefore, it is not possible on this figure to determine the critical spacing factor for ECC with high volume FA, since they were both found to be frost resistant.

Table 4. Freezing and thawing resistance of ECC and ECC matrix

	ECC1 (M45)	ECC2
# of cycles completed	300	300
Change in mass (%)	-1.3	-8.0
Pulse velocity change (%)	-2.2	-4.7

In general, the ECC specimens exhibited some surface scaling at the conclusion of the freeze-thaw cycling (see Figure 1). Reduced surface scaling was observed on the ECC1 specimens compared to ECC2 specimens. This was probably due to the greater maturity (higher compressive strength at the time of testing) of the former test specimens because of lower FA content. The scaling was, however, clearly confined to the surface layers of the test specimens, and had no effect on the integrity of the ECC mass. There are a number of possible explanations for the excellent performance of these non-air entrained ECC samples. A possible reason for the ECC's excellent frost resistance can be attributed to its high ductility under tensile loadings. It is well known that upon freezing, water in capillary pores expands.

If the required volume is greater than the space available, the pressure build-up could reach the tensile strength of the material, resulting in local micro-crack formation, brittle rupture and scaling.

(a) ECC1 after 300 F/T cycles **(b) ECC2 after 300 F/T cycles**

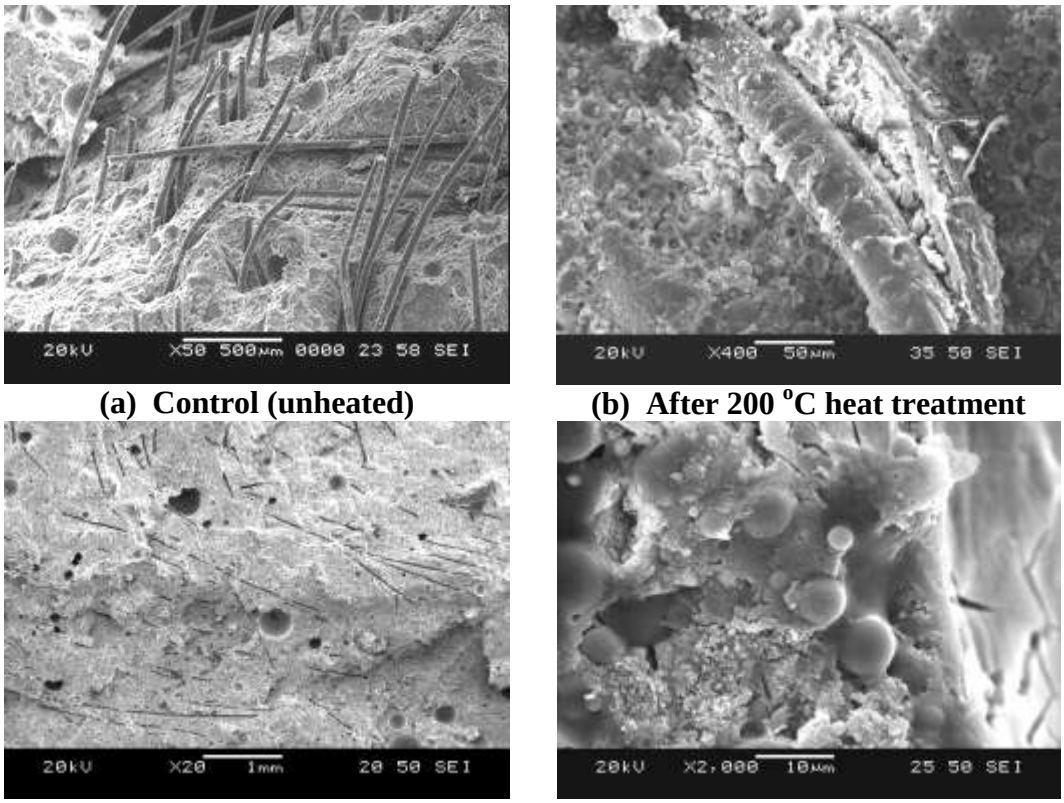
Figure 1. ECC specimen surface appearance after freeze-thaw (F/T) cycles

3.2 Fire Resistance

3.2.1 Microscopy observations

In order to study the behavior of microstructure of ECC after various elevated temperatures, observations with a SEM were performed on samples taken from the cores of 50 mm ECC specimens that had been exposed to a temperature between 200 ^{o}C and 800 ^{o}C for one hour. Figure 2 shows the SEM micrographs of ECC specimens for the unheated specimens as well as the thermally-treated specimens at various temperatures. Figure 2-a shows general view of PVA fibers scattered in a non-heated ECC specimen. Micrographs of the unheated samples consist mainly of ill-crystallized and fibrous particles of C-S-H gel, amorphous and well-crystallized calcium hydroxide and numerous unhydrated FA particles. Figure 2-b shows that the microstructure of the ECC specimen did not undergo significant changes with no apparent cracks after fire exposure at 200 ^{o}C. At 400 ^{o}C, PVA fibers melt completely, creating additional inter-connected pores and small channels in the matrix that can decrease pore pressure inside the ECC (Figure 2-c). As seen in Figure 2-c, PVA fiber dosage is high enough that fibers alone constitute a connected network. Therefore, the use of PVA fiber clearly affects porosity at high temperatures. After exposure to 600 and 800 °C, the morphology of hydration products showed numerous intact FA particles and massive structure of hydration products (especially C-S-H gel); almost all hydration products and silica sand lost their characteristic structure (Figure 2-d), appearing as ill-crystallized or amorphous structures by

losing their characteristic crystal structure. SEM analysis also indicated that beyond 800 ^{o}C, microcracking increased around the grains of unhydrated FA particles.



(a) Control (unheated) **(b) After 200 ^{o}C heat treatment**

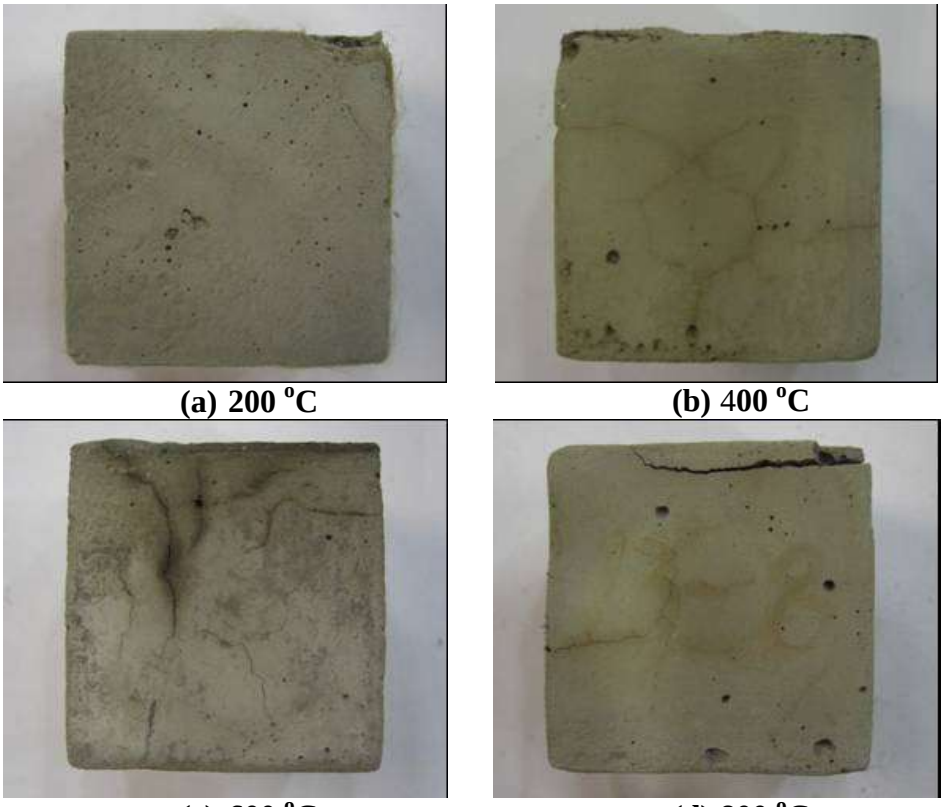
(c) After 400 ^{o}C heat treatment **(d) After 800 ^{o}C heat treatment**

Figure 2. SEM micrograph before and after thermal treatment

3.2.2 Surface and spalling characteristics, and mass loss

In this research study, no explosive spalling occurred after ECC specimens were subjected to air cooling after being exposed to peak temperatures of up to 800 ^{o}C. As explosive spalling is governed by a vapor-pressure mechanism [11], it is reasonable to consider that concrete incorporating PVA fiber can provide a benefit to ECC so as to prevent it from explosive spalling, due to the fact that it is melted under temperature around 230 °C and hence moisture in ECC can escape through inter-connected pores to outside of ECC [11].

Figure 3 shows surface crack patterns of ECC specimens as a result of various elevated temperatures. Cracking became apparent when the exposure temperatures exceeded 400 ^{o}C. In some of the cubes, hairline cracks were observed at 400 ^{o}C (Figure 3-b). At temperatures above 400 ^{o}C, microcracking increased significantly (Figure 3-c and d), first around hydration products and then around grains of unhydrated fly ash and cement.



(a) 200 ^{o}C **(b) 400 ^{o}C**

(c) 600 ^{o}C **(d) 800 ^{o}C**

Figure 3. Typical crack patterns on the surface of ECC cubic specimens after exposure to high temperatures

The deterioration of specimens subjected to various elevated temperatures was also assessed by mass loss measurements. Figure 4 shows the relation between weight loss and temperature of heated ECC and ECC matrix mixtures. As seen in Figure 4, the mass loss increased with increasing exposure temperature, a result which is mainly associated with liberation of free and physically bound water from the decomposition of calcium hydrates and the other formed cement hydrates. At higher temperatures of 600 and 800 ^{o}C, the weight change of ECC was mainly caused by the dehydration of paste and crystal transformation of quartz as discussed in the preceding section. During heat treatment of up to 400 ^{o}C, the weight of the melted fibers also had an influence on mass loss.

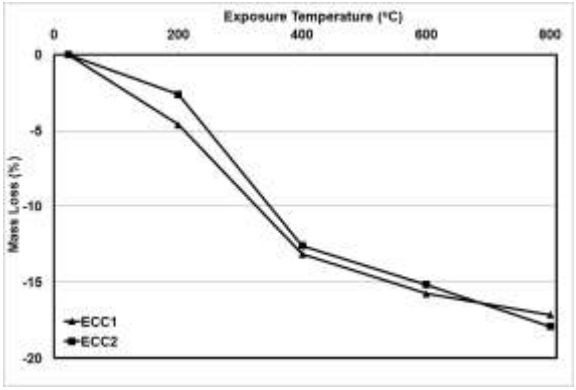


Figure 4. Change in mass loss of ECC mixtures with temperature

4. Conclusions

The objective of this research is to assess the effect of fly ash (FA) on the microstructure, fire and frost durability of the non-air-entrained Engineered Cementitious Composites (ECC). ECC mixtures with two different contents of FA as a replacement of cement (55 and 70% by weight of total cementitious material) were prepared. The results of the investigation can be summarized as follows:

Apart from the slight reductions in UPV and increase in mass loss, the results presented in this study largely confirm the durability performance of ECC material incorporating high volume of FA under frost exposure. Increasing levels of FA lead to higher reductions in the frost durability compared with standard ECC mixture (ECC-1, M45) due to the lower maturity (lower compressive strength at the time of testing). The superior performance of ECC can be explained by higher ductility and strength, and good air-void parameters even without air entraining admixture.

When exposed to high temperatures up to 400 oC, the residual properties of ECC mixtures drops slightly, followed by minimal microcracking on the surface, when compared to values obtained from unheated specimens. Moreover, no spalling occurred after ECC specimens were subjected to air cooling after being exposed to peak temperatures of up to 800 oC. In light of this point, PVA fiber is beneficial to help ECC overcome vapor pressure build-up under high temperatures and hence avoid occurrence of spalling by melting at approximately at 230 ^{o}C. Increasing FA content from 55% to about 70% provide ECC with slightly better residual properties after exposure to temperatures from 200 ^{o}C to 600 ^{o}C. Thus it may be feasible to increase the allowable ‘‘working’’ temperature for ECC by incorporating a high

volume of FA into mixes, which means that a larger proportion of structures exposed to high temperatures can remain serviceable. On the other hand, the effect of the addition of FA diminished when the exposure temperature was raised to 800 ^{o}C.

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