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Design of rapid hardening engineered cementitious composites for sustainable construction

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Abstract

This paper deals with design of environmentally friendly Rapid Hardening Engineered Cementitious Composite (RHECC) nanomodified with ultrafine mineral additives, polycarboxylate ether based superplasticizer, calcium hydrosilicate nanoparticles and dispersal reinforced by fibers. The incremental coefficient of surface activity was proposed in order to estimation of ultrafine supplementary materials (fly ash, methakaolin, microsilica) efficiency. A characterization of RHECC's compressive and flexural properties at different ages is reported in this paper. Early compressive strength of ECC is 45-50 MPa, standard strength – 84-95 MPa and parameter $R_{c2}/R_{c28} - 65-70\%$. The microstructure of the cement matrix and RHECC was investigated. The use of ultrafine mineral supplementary materials provides reinforcement of structure on micro- and nanoscale level (cementing matrix) due to formation of sub-microreinforcing hydrate phase as AFt- and C-S-H phases in unclinker part of cement matrix, resulting in the phenomena of "self-reinforcement" on the microstructure level. Designed RHECC may be regarded as lower brittle since the crack resistance coefficient is higher comparison to conventional fine grain concrete.

Key words: Rapid Hardening Engineered Cementitious Composite, nanomodification, ultrafine additives, polycarboxylate ether based superplasticizer, sustainable development

1 Introduction

Conventional concrete is brittle and tends to crack easily under mechanical and environmental loads, there are concerns with durability. This poses potential danger and limitations of high strength concrete in structural applications. Durability and compliance with the requirements of sustainable development are important goals, therefore current construction practice must undergo a paradigm shift to achieve cost effective concrete structures that are high performance and "crack-free".

Cementitious materials, which are intrinsically brittle materials, can exhibit a degree of ductility when reinforced with a sufficient volume fraction of a fibrous phase [1]. The development of engineered cementitious composites (ECC) – materials reinforced with

specially selected short fibers, that have characteristics of concrete with increased bend capability, high ductility and would be valuable for structural applications [2, 3]. The use of natural fibers as fillers into building material with reinforcement function gains the significant interest in area of development environmentally friendly products in particular fibrous biocomposites [4]. In the case of traditional disperse reinforcement, the problem of inhibition of cracks of only one structural level is solved. While the cracking hierarchy and the complex of cracks indicate the presence of various sizes defects in concrete. Cracks of concrete belong to the appropriate scale level – nano-, sub-micro-, micro-, meso- and macrolevel [5]. The one of innovative way in order to reliably design Rapid Hardening ECC (RHECC) in accordance with principles of sustainable development in the building industry is nanotechnology and nanoscience, which are concerning with the usage of materials falling in range of few to less than 100 nanometers and creating new possibilities to control and improve properties of concretes, systematically engineering of the material at nano-, micro-, and macroscales [6, 7]. The ultrafine particles are characterized by extremely high specific surface area, defined a supply of "excess" surface energy, what can accelerate chemical reactions, determine catalytic activity and cause more substantial influence of superficial atoms on the synthesis of the cementitious systems strength. One of the widely used methods of nanotechnology in the production of RHECC is the modification by the surface active substances of new generation and ultrafine additives [8].

2 Materials and methods

2.1 Materials

The ordinary Portland cement CEM I–42.5 R (OPC) from JSC "Ivano-Frankivskcement" (Ukraine) based on the clinker of normalized mineralogical composition, mass. %: $C_3S - 64.20$; $C_2S - 12.88$; $C_3A - 5.65$; $C_4AF - 14.62$, was used in the investigation. Low-calcium fly ash, highly active metakaolin and silica fume were used as supplementary cementitious materials (SCMs). The content 10.0; 50.0 and 90.0 vol.% of OPC particles is equal to 5.75; 19.42 and 56.29 µm, respectively (Table 1). The value D_{10} for fly ash, metakaolin and silica fume are correspondingly 9.01, 2.2 and 0.07 µm. The particle size allocates roughly meets the requirements of the gap-graded particle size distribution in cementitious systems.

Material	D ₁₀ , μm	D ₅₀ , µm	D90, µm
OPC	5.75	19.42	56.29
Fly ash	9.01	40.21	46.59
Silica fume	0.07	0.15	0.30
Metakaolin	2.2	10.30	13.7

Table 1: Particle size distribution of Portland cement and SCMs

The polyfraction sand was used for cementitious composite production. Grain size distribution of polyfraction sand fulfills demands of EN 196-1 to CEN-Standard sand. An innovative second generation of polycarboxylic ether polymers superplasticizer GLENIUM ACE 430 (PCE), as well as the admixture X-SEED 100 (BASF), which contains CSH-

nanoparticles, were used for nanomodification of cementitious systems. Degree of dispersed reinforced of engineered cementitious composite was 0.5 %.

2.2 Methods

The particle size distribution of Portland cement and mineral additives was determined by a laser granulometer Mastersizer 3000. Consistency of fresh concrete was determined by flow-table method conforming EN 1015-3 standard. The fine-grained concrete components were mixed according to EN 196-1 procedure. The samples 40 mm x 40 mm x 160 mm were cured in normal conditions for hardening of concrete (90-100% RH at $20\pm2^{\circ}$ C). After 2, 7 and 28 days the samples were samples underwent the compressive and flexural strength tests according to EN 196-1. The impact strength test of RHECC was determined using the pendulum mechanical copper MK-0.5. Scanning electron microscopy (SEM) was used to investigation of microstructure cement matrix and RHECC.

3 Results and discussion

To evaluate the interfacial surface of mineral components coefficient of surface activity K_{sa} was calculated as the ratio of the surface area of the particles to their volume. Thus, for the particles of Portland cement of average size 19.42 µm K_{sa} is 0.31 µm⁻¹, for fly ash with an average size of particles 8.71 µm K_{sa} =0.69 µm⁻¹. The K_{sa} value of highly active metakaolin for D₅₀=10.3 µm is 0.58 µm⁻¹ and K_{sa} of microsilica with average particles size 0.15 µm is 40.0 µm⁻¹. The incremental coefficient of surface activity (determined by multiplying the coefficient of surface activity by the content of each fraction of the material) was proposed in order to estimation of ultra-fine supplementary materials (fly ash, methakaolin, microsilica) efficiency [7]. The maximum value of incremental coefficient of surface activity K_{isa} of fly ash, highly active metakaolin and microsilica is 10.1; 15.82 and 531.8 µm⁻¹ vol. % respectively, whereas for CEM I-42.5 is 3.81 µm⁻¹ vol. %. Estimation of value of surface activity coefficient shows that interfacial surface is determined mainly by the particles of size less than 1 µm.

Rapid adsorption of the molecule of polycarboxylate superplasticizer MasterGlenium ACE 430 onto the nanoparticles, combined with an efficient dispersion effect, exposes increased surface of the cementitious compositions to react with water. Compressive strength of ECC from high flowability mixture after 2 days is 45-50 MPa and after 28 days – 84-95 MPa and parameter $Rc_2/Rc_{28}=65-70\%$, that allows regarded them to rapid hardening and high strength composite (Figure 1).



Figure 1: Compressive strength of ECC

The enhancement of early strength of RHECC could be related with efficient dispersion effect of polycarboxylate ether based superplastisizer and important microstructural aspects: the packing effect, heterogeneous nucleation and pozzolanic reaction of nanoparticles. The modification of ECC cement matrix by suspensions of calcium silicate hydrate (C-S-H) colloidal particles (Master X-Seed hardening accelerator) and PCE causes a significant acceleration of the early hydration kinetics. Due to a seeding effect the C-S-H nano-additives provides homogeneous nucleation in the pore solution between the cement particles. They can act as internal reinforcement as well as nucleation and crystallization seeds.

The crack resistance coefficient (ratio of flexural strength to compressive strength) of RHECC is 0.225-0.245 at early age and 0.171-176 after 28 days. Designed RHECC may be regarded as lower brittle since the crack resistance coefficient of conventional fine grain concrete is 0.204 and 0.162 after 2 and 28 days, respectively (Figure 2).



Figure 2: Crack resistance coefficient of RHECC

The energy expended to the destruction of RHECC under impact load is 1.2 kJ/m^2 and 1.6 kJ/m^2 after 7 and 28 days, respectively. Substantial absorption of the impact energy is provided by increasing of the bond and adhesion of the fiber with the cement matrix, forming a dense layer of hydrates in the contact zone and forming a homogeneous non-defective structure of the composite. As can be seen in Figure 3a the fiber surface displays cementitious materials that have been partially destroyed.



Figure 3: SEM pictures of RHECC (a) and RHECC cement matrix (after 28 days)

The nanomodification of RHECC with ultrafine supplementary materials and C-S-H nanoadditives provides reinforcement of structure on micro- and nanoscale level due to forming of AF_{t-} and C-S-H-phases of needle and fibrous habitus in unclinker part of cement composition resulting in the phenomena of "self-reinforcement" on the microstructure level. The modification of RHECC with dispersed fibers provides the averaging of the elastic properties of the components of the system, herewith the defects and cracks of micro- and mesoscale level disappear and strength of composites.

4 Conclusion

Engineered cementitious composites represent a new concrete material that offers significant potential to reduce the durability and sustainability problem of concrete construction. The improving of RHEEC performance is reached by hybrid reinforcement of their structures at the micro level – by energy-active ultrafine mineral additives, as well macro level – by dispersed fibers. The incorporation of nano- and ultrafine particles, which are characterized by high specific interfacial area and "excess surface energy", into the cement matrix provides directional control of structure formation at the early age of the cement hydration, performance and durability of hardened cementitious composites.

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