CEMENTITIOUS COMPOSITE MATERIALS WITH IMPROVED SELF-HEALING POTENTIAL

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ABSTRACT

Cement-based composites have proved, over the time, certain abilities of self-healing the damages (cracks and especially microcracs) that occur within their structure. Depending on the level of damage and of the composite type in which this occurs, the self - healing process (SH) can range from crack closing or crack sealing to the stage of partial or even complete recovery of material physical - mechanical properties.

The aim of this paper is to present the general concept of Engineered Cementitious Composites (ECCs) with their unique properties including their self-healing (SH) capacity, as an innovative direction for a global sustainable infrastructure.

The experimental steps initiated for the development in Romania of this unique category of materials, using materials available on the local market, are also presented.

Keywords: cementitious materials, self-healing (SH) mechanisms, crack control behavior under loads

REZUMAT

Materialele cementoase pe bază de liant hidraulic au dovedit pe parcursul timpului o anume abilitate proprie de a se autovindeca, respectiv fisurile şi, cu precădere, microfisurile ce se formează în masa lor. Depinzând de gradul de degradare şi de tipul de compozit în care acesta se produce, procesul de autovindecare (SH) poate evolua de la închiderea, respectiv sigilarea fisurilor şi până la stagiul de recuperare parţială sau chiar totală a proprietăţilor fizico-mecanice.

Scopul acestei lucrări este prezentarea generală a Materialelor Cementoase Compozite, respectiv ECC (Engineered Cementitious Composites) şi caracteristicile lor unice de inducere, incluzând abilitatea de autovindecare, totul ca o direcţie inovativă în trendul general al conceptului de sustenabilitate globală a infrastructurilor.

De asemenea sunt prezentaţi paşii incipienţi, experimentali, pentru dezvoltarea acestor compozite pe teritoriul României, utilizând materie primă de provenienţă locală.

Cuvinte cheie: materiale cementoase, mecanisme de autovindecare (SH), controlul fisurării sub solicitări

1. INTRODUCTION

Cement based composites, the most used building materials all over the world, have proved to be very vulnerable to inherent cracking, caused by several and various causes as: low tensile strength, early age cracking due to hydration processes, poor casting or inappropriate structural design, etc. Moisture, meaning water under different states, liquid, solid or vapour, can freely migrate through these interconnected paths, enlarging them and, as consequence, weakening the structural capacity of concrete elements, facilitating corrosion of reinforcement and complex forms of chemical and physical attack.

As a balance to the crack vulnerability, concrete and generally, cementitious materials showed along the time certain ability to heal the damages (cracks) that occur within their structure.

The autogenous self-healing capacities of cementitious materials were remarked at a scientific level starting with the French Academy of science in 1836 [5]. Considered from an objective and realistic perspective, they may have an important economic impact on service life extension, at minimum, costs of concrete infrastructure and, at the same time, in the reduction of maintenance activities. Implicitly, economic and ecological gains will occur, by the reduction of pollution, of energy consumption and of CO_2 emissions.

2. AUTOGENOUS HEALING OF CONCRETE

Along the time, by experimental or theoretical investigations, it was shown that concrete cracks can seal in time, as a direct consequence of some complex mechanisms [8]: a) unhydrated cement particles, due to continued hydration can develop new calcium silicate hydrate (C-S-H) in the matrix; b) the precipitation of calcium carbonate ($CaCO_3$) is considered to be the most important mechanism of crack healing: the calcium ions (Ca^{2+}) present in the cement matrix must react with the carbon dioxide (CO_2) or with the hydrogen carbonate (HCO_3) – existing in water – in order to precipitate ($CaCO_3$). Edvardson [3] concluded that the mechanism of $CaCO_3$ forming in the concrete crack depends on the width of the crack and water pressure and does not involve other parameters like water hardness and the concrete composition.

It was concluded that, generally, the self-healing of concrete involves a combination of the above mechanisms, together with the C-S-H swelling in the crack and the cement particles ability to migrate into the cracks, blocking them [4].

Yang [11] considers that there are some essential environmental or material properties for autogenous concrete cracks to develop a healing process: 1) the specific chemical ions, as calcium ions, should be present in the concrete matrix; 2) the environment should ensure the necessary humidity (e.g. alternate air- water, water immersion etc.); 3) the crack width should be as small as possible, ranging from <50 μm (for complete healing) to a maximum of 150 μm for a partial crack closing. Small cracks imply that, besides their sealing and preventing the ingress of exterior aggressive agents like saline water, acid rain and carbon dioxide to enter the matrix and corrode it, they induce possible recovery of initial mechanical and physical properties of the material [9].

2.1. Self-Healing - General approaches

Along the time, innovative approaches were considered in order to determine self-healing mechanisms development in various types of cementitious matrices. Apart from the classical methods of inducing moisture into the concrete matrix in order to obtain the mentioned healing compounds, the concept of intelligent material was introduced, referring to microencapsulation [13] or to the use of pipettes (hollow fibers) [2] containing several types of curing agents, ready to be released into the crack when necessary.

The use of expansive agents (e.g. geo-polymers) and mineral admixtures was considered to intensify the formation of cementitious products [14].

The use of $CaCO_3$ precipitating bacteria in the concrete matrix is an interesting approach developed by research groups in Delft and Ghent [1], [10].

The incorporation in the cement matrix of shape-memory alloy or shape-memory polymers represents another new and innovative direction in the field of self-healing materials, with promising results for micro-sized cracks, including mechanical properties recovery [14].

3. ENGINEERED CEMENTITIOUS COMPOSITE (ECC)

Another possible strategy for accelerating the occurrence of the self-healing phenomenon, as a preventive approach for structure durability, consists in developing cement-based compositions with improved self-healing potential, besides the required physical, mechanical or chemical characteristics.

An eloquent example in the field is represented by Engineered Cementitious Composites (ECCs), which represent a new type of cement-based materials, characterized by unique microcrack behavior, as compared with traditional cementitious materials, and which leads its superior capacity of self – healing.

3.1. ECC – Theoretical Design and Crack control

Engineered Cementitious Composites (ECCs) were developed in order to counter – besides the brittle behavior of concrete matrix under loading, achieved in case of Fibre Reinforced Concrete (FRC) – the lack of ductility that is specific to cement-based compositions.

ECC represent a unique composite material from the High-Performance Fiber-Reinforced Cementitious Composites (HPFRCC) category, designed under the micromechanical crack control principles, considering the interactions between the fiber and the matrix. The goal is to achieve the strain-hardening, metal-like behavior of the material under tensile loading, different from the tension-softening response of FRC (Fig. 1).

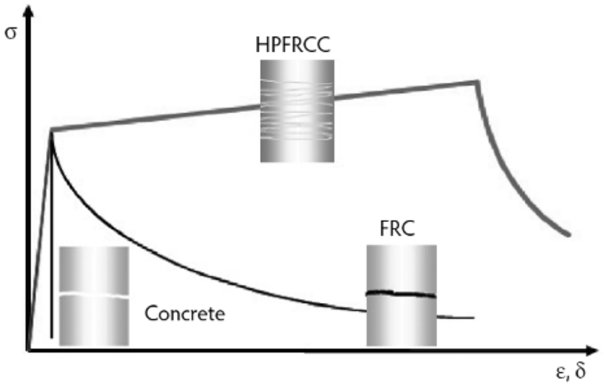

Fig. 1. Uniaxial tensile stress–deformation relation: C, FRC and HPFRCC [6]

Crack control design, keeping the crack widths less than 60 μm even in case of large deformations, ensures the strain-hardening response, i.e. the capacity of still carrying higher loads and developing increased deformations, after the moment of the first crack occurrence (Fig. 2). The fibers in the ECC matrix show a slip-hardening behavior and a decreased chemical bond to the cementitious matrix, which induce the occurrence of new cracks under increased loading. This type of response under loading is different from the tension softening one, which is characteristic for FRC: i.e. the initial crack enlarging and the capacity of tensile loading experiencing a sudden drop (Fig. 1).

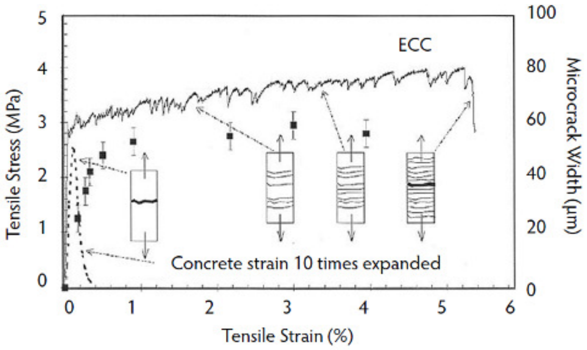

Fig. 2. Uniaxial tensile stress–deformation relation: concrete, FRC and HPFRCC [6]

Experimental procedures [12] showed the tight crack width control of ECC: under loading, at around 1% strain, the microcrack widens up from 0 to 60 μm. Above that strain value, under continued loading, new, similar type cracks will appear, none growing above 60-80 μm. This behavior is considered a steady-state crack width of the material and is assumed to be an intrinsic property of the composite, not depending on adjacent factors: loading conditions, geometry, dimension or steel reinforcement ratio of the element [6].

3.2. ECC – Tensile and Compressive Characteristics

The physical and mechanical characteristics of ECC can be “tailored” by the means of micromechanics, according to the desired domain of use.

The classical mix designs developed till the present days [6] do not offer high compressive strengths, the usual values range from a moderate 20MPa to 95 MPa.

The flexural capacity is strongly related to the multiple microcracking development, inducing the strain hardening response under loading, which leads to the name of “bendable concrete”. The flexural capacity is 10 to 15 MPa, associated to a corresponding tensile strain of more than 5%, which means several hundred times more than of usual concrete characterized by brittle failure (Fig. 2).

3.3. ECC – Self-healing capacity

The crack width around 60-80 μm characteristic for ECC behavior under loading signifies much smaller cracks than those in regular concrete or generally cement-based materials and consequently improvement regarding the structural durability; at the same time, the small crack interval ensures fulfilling the Yang's third condition for self-healing development, i.e. a controlled tensile crack width, limited to the 0 – 150 μm range [11]. Thus, ECC proves itself to be a composite with intrinsic self-healing potential of its matrix.

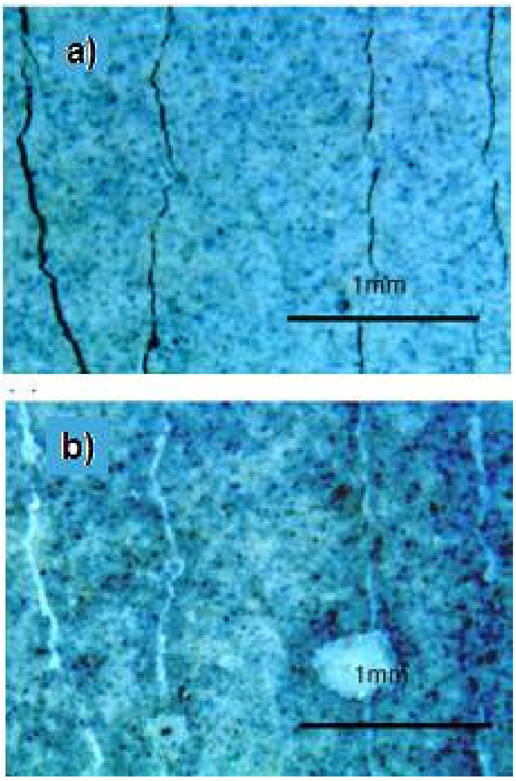

Fig. 3. Microcracks in ECC specimen: a) before SH; b) After SH [12]

Experimental procedures, consisting in ECC specimens subjected to loading until a certain state of cracking was induced, were subsequently exposed to different curing, environmental-like conditions: wetting and drying cycles, water immersion etc. [12]. The tests showed encouraging results: complete sealing of microcracks (Fig. 3) and even recovery of mechanical and transport properties. It was concluded that, besides tight crack control, the consistent amount of fly ash in the ECC composition, meaning an increased pozzolanic activity in the matrix, induced self-healing products via continued hydration processes; the low water/binder ratio helped the mechanism [10], the tensile stress showing a sudden drop (Fig. 1).

We can conclude that ECC, due to its unique combination of intrinsic properties, has the ability to develop effective self-healing in the natural, environmental conditions, although further research is necessary in the area [7].

4. EXPERIMENTAL APPROACH

4.1. Main Objectives

The main objective of the theoretical and experimental research was the development of reliable mix designs of cement-based composites, Self-Healing Fiber Engineering Cementitious Materials (SH – FECM), having the main characteristics, both in fresh and hardened state, similar or close to those of ECCs, including the self-healing (SH) potential. The challenging part is using the local raw materials, available on Romanian or Southern European market.

The starting point for the SH – FECM mix design development was considered the classic ECC M45 [6], containing Portland Cement and Type F fly ash as the binding system, in approximately equal proportion; a low water/binder (w/b) ratio of 0.26 was maintained by using an efficient High-Range Water Reducer (HRWR) admixture (polycarboxylate composition), which ensured the creamy texture with proper self-consolidating characteristics of the fresh composition. As aggregate, fine silica sand was used, having the maximum grain size of 250 μm. Several types of fibers, namely polyethylene (PE), or Polypropylene (PP) can be used for the ECC mix design, but for ECC M45 there were used polyvinyl alcohol (PVA) fibers (2% by volume, with raised tensile properties of 1600 MPa.

4.2. Materials

Four initial mix designs were established, using mostly conventional materials with large local availability.

The binding compounds included Portland Cement, namely CEM I 52.5 R and Govora fly ash, a certified product with the dry bulk density of 1790 Kg/m3 and the index of pozzolanic activity of 78,59 %, established at the age of 90 days, according to the corresponding technical sheet.

Table 1. *Design proportions*

Mix Design	I	II	III	IV
Materials	**Mix design proportions**			
Cement (C)	1	1	1	1
Fly Ash (FA)	1.2	1.2	1.2	1.2
Binding system (C + FA)	2.2	2.2	2.2	2.2
Silica sand (max grain of 500 μm) (S)	0.8	0.8.	0.8	0.8
Water (W)	0.79	0.82	0.76	0.75
HRWR admixture	Type 1	Type 1	Type 1	Type 2
	0.04	0.04	0.05	0.04
Liquid (W+ HRWR)	0.83	0.86	0.81	0.79
Fibres (F) volume %	2	2	2	2
W/C	0.79	0.82	0.76	0.75
W/B	0.36	0.37	0.35	0.34
L/C	0.83	0.86	0.81	0.79
L/B	0.38	0.39	0.37	0.36

The aggregates consist in silica sand with the maximum grain size of 500 μm, provided by a local producer from Cluj-Napoca area. The grain size dimension exceeds the recommended values, but it was assumed proper for the first test batches.

Two types of HRWR polycarboxylate admixture were used: Type I for the first three mixes and the second type for the last mix, which proved to be more efficient regarding the fresh state properties of the material (see Table 1, specific ratios).

Polypropylene (PP) fibers were used, characterized by a tensile strength of approximately 500 MPa and length/diameter ratio of 50, according to relevant data from the producer's technical data sheet.

The proportions of the four mixes and other relevant data are presented in Table 1

4.3. Mix Design

The four mixes were established considering, as constant parameters, the binding system (the quantity of cement and fly ash), the silica sand amount and type and fiber amount (Table 1).

The variable parameters were: the total liquid amount in the mix (HRWR admixture and the water), with direct consequence over specific ratios (presented in table 1) – for the last mix a different type of HRWR was used – and the mixing sequences and their specific durations.

Regarding the sequence of operation, the mixing procedures proved themselves to different from those specified by [6], considering that the test batches involved 0.8 l material and that they were obtained using a small mortar mixer, according to the EN 196-1 [15] specifications.

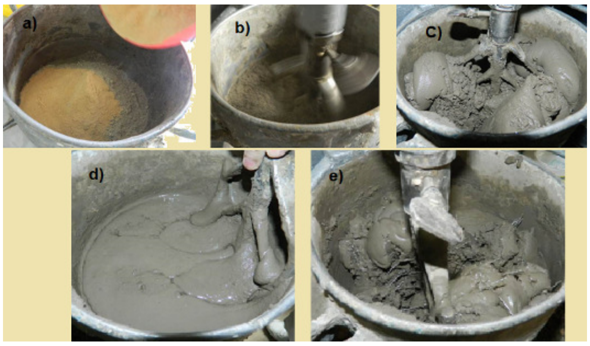

Fig. 4. Mixing sequences: a) dry mixing of binder (C+FA) and sand; b) Partially wet mixing; c) Mix without fibers; d) Mixing break; e) Fibers addition in the mix

Relevant mixing steps and also the aspect of the fresh compositions are presented in Figure 4.

5. RESULTS AND DISCUSSIONS

The first experimental SH-FECM mix design provided some interesting results and offered new paths for future research in the field of ECC's development.

5.1. Fresh State Mixes

The fresh state materials have a creamy, plastic texture. The first two mixes show self-compacting properties (Fig. 5) but their liquid content (water and HRWR) is also more increased in comparison with the third and the forth mix (Table 1). The consistence of fresh material was analyzed using flow table. It should be noted that no shocks were applied to the first two, self-consolidating mixes.

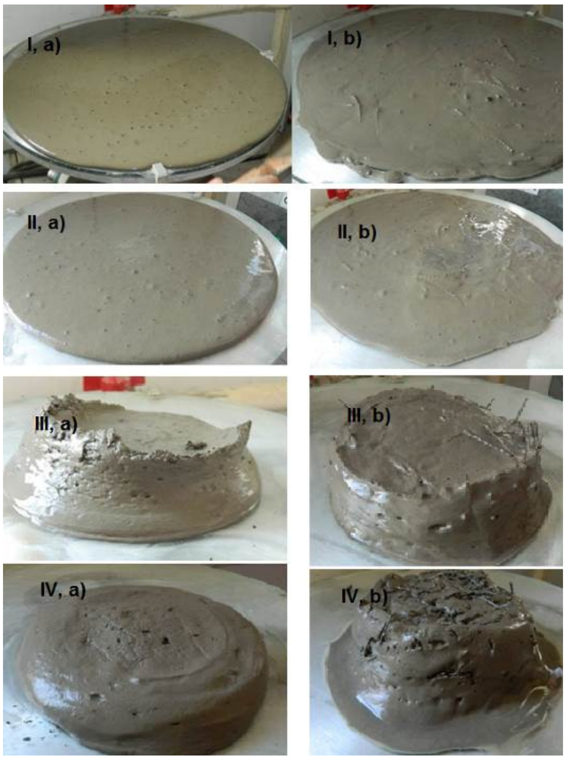

Fig. 5. Fresh state materials: I, II, III, and IV mixes: a) without fibers; b) with fibers

The fourth mix showed reasonable consistence parameters at the optimum L/B ratio; as a consequence the HRWR admixture was considered more appropriate for future investigations.

The visual analyses of the composites show a matrix-fiber incompatibility (the fiber dimensions – diameter and length – seem to be too large for such a smooth matrix; the interfacial connection between fibers and the matrix is considered improper (Fig. 5).

5.2. • Flexural and Compressive Properties

The flexural and compressive characteristics of the cement-based materials were determined according to EN 1015-11 [16].

Fig. 6. Flexural test: a) specimens before tests; b) flexural loading; c) and d) rupture; e) fiber distribution in the matrix

The three point bending test was performed at the age of 28 days and then the compressive strength was determined on half-prisms resulted after the bending test (Fig. 6).

The specimens, 40 x 40 x 160 mm prisms, were removed from the moulds after 24 hours; the subsequent curing included 7 days water immersion, at (20 ± 2)°C temperature and then exposure to the air, at RH (65±5)% and T (20±2)°C, in accordance to natural environmental conditions.

The flexural and compressive results are presented in Table 2.

Table 2. *Flexural and Compressive Results*

MIX		f_{ti}* [MPa]	f_{ti} [MPa]	$f_{ti,av}$ [MPa]	$f_{c,av}$ [MPa]
MIX I	I/1	-	14.7	18.7	61.3
	I/2	7.7	21.3		
	I/3	6.8	20.1		
MIX II	II/1	4.8	12.8	13.5	62.1
	II/2	4.5	16.2		
	II/3	5.6	11.5		
MIX III	III/1	5.2	20.9	18.3	68.8
	III/2	4.0	17.0		
	III/3	7.1	17.0		
MIX IV	IV/1	4.9	11.3	13.8	70.,5
	IV/2	7.5	15.4		
	IV/3	7.7	14.8		

In the table:

f_{ti}^*	three point bending strength, at first crack [MPa];
f_{ti}	three point bending strength, [MPa];
$f_{ti,av}$	average value for three point bending strength, [MPa];
f_c	compressive strength, [MPa];
$f_{ti,av}$	average value for compressive strength, [MPa];

The flexural and compressive tests performed on prismatic specimens show good results, despite the fact that further adjustments in the mix design have to be performed; the multiple microcrack behavior under loading, characteristic for ECCs, was not achieved for the moment. The flexural strength showed increased values. The improvement due to fibers addition is obvious, but the first crack enlarges under loading leading to failure, without reaching the strain hardening effect, as desired.

The compressive results ranging from 60 to 70 MPa are according to the anticipations.

6. CONCLUSIONS

The first steps of theoretical and experimental approach in the topic of fiber cementitious composites with microcrack behavior under loading show promising results but also suggest the need of further research and experimental design mixes. Despite the fact the flexural strengths of the composites have high values, the microcracking state, the key towards self-healing improved matrix, is still not reached.

Further steps imply changes regarding the compound materials: a) the fiber type should be varied in order to improve the compatibility with the cementitious matrix; b) the workable life of the composites should also be modified, in order to have better self-consolidation of the fresh material; for the time being the second type of HRWR polycaroboxylate admixture, used for the fourth mix, is considered more appropriate, offering lowest L/B ratio, and it is considered for future use in the procedures to come; c) a considerable reduction of the L/B ratio, closer to the original provisions, must be gained.

Further investigation are intended in order to demonstrate the self-healing capacity of the cementitious mixes, considering both crack sealing and eventual recovery of mechanical and physical characteristics.

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