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POLYMERIC COATED REACTIVE GRAINS AS INTELLIGENT ADDITION IN CEMENTITIOUS COMPOSITES FOR GENERATING THE SELF-HEALING EFFECT

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Rezumat. *Cerințele de implementare stringentă a criteriilor dezvoltării durabile, pe fondul poluării masive, a necesității conservării resurselor naturale și de protejare a mediului, imprimă necesitatea dezvoltării unor materiale de construcții cu performanțe superioare, atât din punct de vedere al materiei prime utilizate și a costurilor de producție, cât și a caracteristicilor fizico-mecanice și de durabilitate pe durata de viață a structurii. Astfel, stimularea caracterului intrinsec de autovindecare autogenă a compozitelor cu matrici pe bază de ciment, pentru creșterea durabilității și duratei de viață simultan reducerii acțiunilor de reparație și mentenanță, reprezintă o direcție de cercetare inovativă, actuală și de anvergură mondială. Prezenta lucrare prezintă direcțiile preliminare, conceptuale și de dezvoltare aplicativă, a unui adaos inteligent de granule reactive cu încapsulare polimerică, destinat materialelor cementoase, respectiv optimizării durabilității acestora prin stimularea potențialului de hidratare continuă, specific acestora.*

Abstract. *The requirements for the stringent implementation of sustainability criteria for development, considering the worldwide context of massive pollution, the need to preserve the natural resources and the urge for environmental protection emphasize the drive for developing high-performance building materials, both in terms of raw materials used and low production costs, as well as related to their physical-mechanical and durability characteristics along the lifespan of the structure where used. Consequently, stimulating the intrinsic self-healing ability of cementitious composites, aiming both, the increase of durability and structural lifespan expansion with simultaneous reduction of*

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repair and maintenance activities, represents an innovative, highly explored, contemporary global research direction. This paper presents the preliminary direction concerning the theoretical investigation and the applicative development of an intelligent addition of reactive grains with polymeric encapsulation, for cementitious materials, namely for optimizing their durability by stimulating the long-term continuous hydration.

Keywords: reactive grains, cementitious composites, Self-Healing effect; continuous hydration, sustainability

1. Introduction

Cracks occurring inevitably in concrete, mortar and cementitious composites represent the damage produced within their micro-structure; therefore, the healing, respectively the self -healing of cement-based materials is entirely related to crack closing (sealing), this phenomena leading to the desired, complete or partial recovery, with respect to the initial state.

It is a fact that concrete and generally cement-based materials represent the most widely used building materials at the global level, experiencing a continuous development and expansion of their use, especially since the Portland cement was discovered in the mid-19th century. Subjected to unavoidable time degrading behavior, the usual design life for a typical concrete structure ranges from fifty to a hundred years; the expected service life is kept functional by the means of consistent activities regarding the building monitoring and repair intervention when the case, which determines worldwide impressive consumption of resources (material and energetic, human labor, economic, etc.). For example, specific evaluations provided a few years ago showed the annual US required budget for maintenance and repair clearly exceeds the one for new structures [1]. The Institution of Civil Engineers of Cardiff University report [2] reveals a similar situation in UK by the means of a relevant, economic (billions of pounds) ratio between repair and maintenance works for concrete structures and new construction works, referring to the Great Britain status for the 1997-2007 period (see Figure 1). Another issue is related to the durability of concrete infrastructure repair: there are evaluations performed in US revealing that approximately 50% of repairs require re-intervention and supplementary efforts for re-repair, which generates an unsustainable character of this approach [3]. Consequently, a change of perspective was considered.

Recently, the ability of concrete structures to repair itself, with reduced or even without help provided by men, has gained a lot of ground in the research communities all around the globe. First scientific observation regarding the intrinsic ability of concrete cracks to seal by themselves, namely Autogenous Healing, was attributed to the French Academy of Sciences, in 1836 [4].

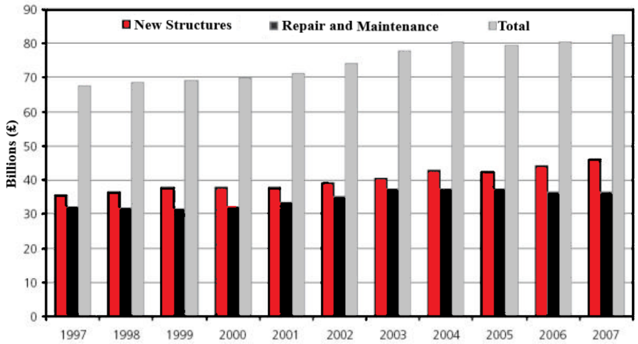

Fig. 1. Comparative evaluation concerning the UK (period 1997-2007):
New Structures vs. Repair and Maintenance [4]

A relevant retrospective on the collective scientific research along the years, in the field of development and analysis of materials with self-healing properties, has happened is provided by Van Tittelboom and De Belie in 2013 [5]. Artificial materials, with properties stimulating the self-healing processes (SH) of damages occurring within their own microstructure, are mentioned for the first time in 1969. In 1979 and then in 1981, there were publications referring to the SH capacity of thermoplastics and composite systems, cross-linked. The first research specifically directed towards concrete and cementitious materials was performed by Dry in the 1990s [6]. The critical moment, which will determine an exponential increase of the interest attached to this topic, was the publication in the journal Nature, in 2001, of White's research [7]. The graphical representation (see Figure 2) regarding the evolution of scientific research and implicitly, of publications related to materials with Self-Healing capacities, hereinafter referred to as SH materials, emphasizes the second half of the 20th century as a crucial period for this topic. Most of research performed till now in the topic of Self-Healing Concrete was focused on understanding the basic mechanisms that are generating the healing effect and also the essential influencing factors (external – environmental, compositional, etc.), in order to be able to optimize the repairing capacity and design principles for cementitious materials with high performance, tailored in agreement to the specific requirements of each structure. Most experimental programs were focused on small scale specimens and lab testing. Still, recent years showed the viability of the concept and its transition towards industry and large-scale projects.

Full size applications are just emerging from consortiums' proposals: a relevant example is represented by the ReSHEAliance, a Horizon 2020 project considered for a period of 4 years, namely 2018-2022; the major aim is developing the Ultra High Durability Concrete UHDC and evaluation of its behavior in real, large scale structures [8].

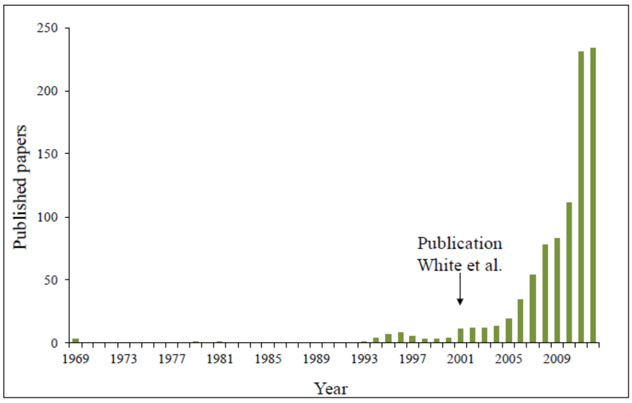

Fig. 2. Evolution of scientific publications related to the topic of Self-Healing materials [5]

Considering all the previous mentioned considerations, we can assume that the Self-healing capacity of concrete, as intrinsic material characteristic, could considerably be exploited and improved in such way to determine the increase of structural durability, overall performance and even service life extension, with reliable reduction of classical activities ensuring the functionality and safety characteristics along the building estimated life cycle. The overall Self-Healing concrete approach, built on resource saving and friendly environmental directions, agrees to the sustainability principals as mandatory requirements for future development in all the fields concerning human life: Industry and Agriculture Social and Political, Environmental and Urban planning, etc.

2. Cracks in concrete

Concrete cracks can occur during any of its life stages, generated by a superposition of factors, external and internal as well (see Figure 3).

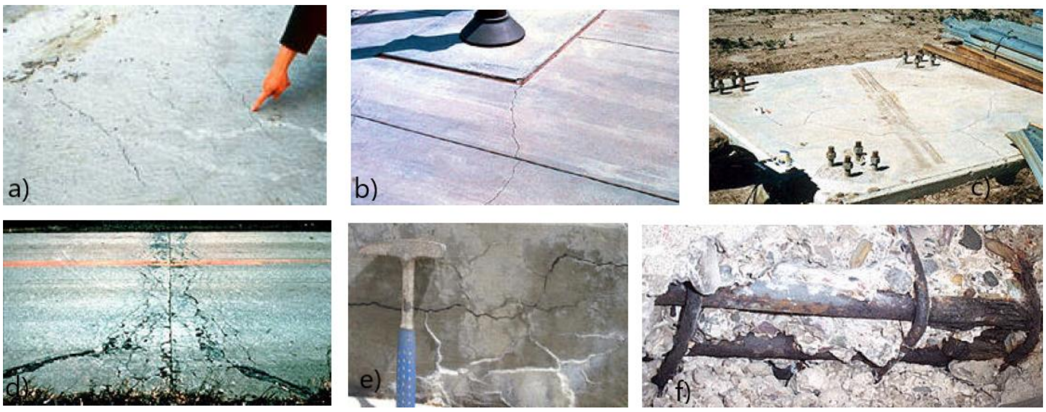

Fig. 3. Crack causes in concrete and their effect: a) Plastic shrinkage; b) Drying shrinkage; c) Thermal effects; d) Freeze-thaw action; e) Aggregate to alkaline reaction (AAR); c) Corrosion of reinforcement [2]

The external causes can be various, ranging from poor both, design and/or construction execution, subgrade settlement due to defective soil bearing capacity evaluation, excessive loading, to environmental factors (harsh weather conditions, like freeze -thaw) and aggressive conditions (favoring the chloride ingress or sulfate attack, carbonation, etc.).

The internal factors mainly refer to concrete's own composition, which, for example, may generate Aggregate to alkaline reaction (AAR) (see Figure 3, c), proved to be lethal. On the other hand, concrete compositional heterogeneity represents the source for cracks and damage. There are several types of compositional heterogeneity within cementitious materials:

1) Dimensional heterogeneity [2]: concrete and cementitious composites represent materials containing *nanoscale particles* (egg. the hydration products (nanoscale), such as calcium-silicahydrates (C-S-H)), *(microscale) particles* (egg. cement particles or fine powder additions) and mesoscale particles (egg. Aggregates or/and fibers, etc.).

2) Mechanical heterogeneity [9]: aggregates' stiffness (expressed by Young's modulus) is highly superior to the stiffness hardened cement paste Young's modulus;

3) Chemical heterogeneity [2, 9]: during the setting and hardening period, the cement paste experiences a contraction generated by chemical causes, strongly obstructed by the granular material. When the heat curing is applied, the thermal expansion coefficient of the cement matrix is three times lower than of the quartzite granules, determining the inherent cracking of the hardened cement paste due to the obstruction generated by aggregate dilatation.

Consequently, plastic shrinkage, drying shrinkage, thermal contraction, freezing and thawing represent generic factors generating concrete cracks, based on the heterogeneousness of its composition.

Micro-cracking of concrete (see Figure 3) is generally unavoidable and usually it does not involve the structural 'failure'. Still, in time, it can bring huge damages to the overall structural performance, especially in terms of durability, as cracks represent real pathways for the aggressive agents (carbon dioxide, saline water, acid rain, etc.). Their consequences lead to crack width increasing and further, to substantial reduction of durability and structural integrity.

3. Self-healing concrete

Generally, self-healing is defined as the *property of a material to develop repair (recover) of damages that occurred within its structure [10].*

Evaluated in accordance to the biomimetic trends, Self-healing (SH) in cementitious composites works on principles similar to living tissues (see Figure 4), with real abilities of physical regeneration and therefor even of functionality, partially or completely, when comparing to the initial state (Virgin state) and also considering the magnitude of the degenerative causality.

Fig. 4. Self-Healing Concrete: associating the phenomenon with the healing of living tissues [11]

The general terminology of the concept of Self-Healing (SH) in the field of cementitious materials includes several directions and approaches: own guidelines and specific definitions have been established as a result of research directions, methods used and results obtained by major research centers in this topic: Japan, Belgium and the Netherlands, Great Britain, USA, etc. The overlapping of developed terminology, definitions and classifications lead to some out-of-phase or mismatches; in order to solve this, the RILEM 221-SHC Technical Committee proposed a unitary set of definitions, for a clear and unitary illustration of the concept [10] (the report "Self-Healing Phenomena in Cement-Based Materials"). More recently, a general evaluation of the specific typologies, intrinsic or stimulated, for inducting and optimizing the SH mechanisms efficiency in cementitious composites, was provided by the review report of the COST Action CA 15202, "Self-healing as preventive repair of concrete structures": „A Review of Self-Healing Concrete for Damage Management of Structures". Three distinct directions have been identified [12]:

1. Autogenous and Nonencapsulated Autonomous Self-Healing;
2. Encapsulated Autonomous Self-Healing (Polymers or Minerals);
3. Self-Healing Bioconcrete.

The Autogenous healing of cementitious composites, as base point of the concept, represents the sum of physical, chemical and mechanical processes, produced exclusively by the compositional nature of the material and under the exclusive exposure to the medium conditions, leading to complete or partial closure (into the depth of the crack or superficial, at the opening edge) of cracks generated in the structure of cementitious materials. Autogenic healing can cover both self-sealing (SS) and self-repair (SR) directions [12, 13].

The phenomenon of autogenic curing of cementitious composites was proved to be the consequence of mechanical processes (particles swelling), physical processes (crack filling with fine particles usual present in the water entering the crack) and most important, the chemical processes (continuous hydration and calcium carbonate precipitation [10, 12] (see Figure 5).

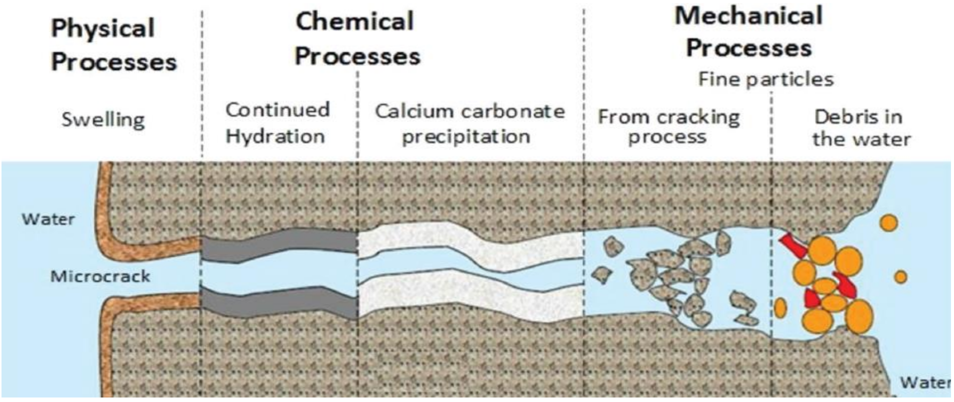

Fig. 5. Self-Healing Concrete: main processes that determine autogenic curing [10, 13]

4. Materials and methods

4.1. Presentation of the concept of polymeric coated reactive grain (PC-RG) addition as concrete Self-Healing promoter in concrete

The *continued hydration* of unhydrated cement grains is considered an essential mechanism of chemical nature, responsible for generating the calcium silicate hydrates gels (CSH), superior to that of calcium carbonate precipitation: they are not able just to seal the crack, but by the means of a high bond strength to the crack walls, they may generate the mechanical recovery of the material, as well [10, 11, 12, 13]. The Continued hydration process was proven to considerably lose its intensity, in time, due to unavoidable consume of unhydrated clinker nuclei, the source for further hydration products. Another aspect relates to the cement production nowadays, based on fine clinker grains contents, with fast initial reactivity in order to reach the full-strength potential at the age of 28 days. After the peak is reached, the hydration process experiences a sudden drop in the continuous hydration process, as the reactive basin is consumed.

This lack represent the fundament of the present research concept, as it can be compensated by a certain reactive grain addition, polymeric coated for reactivity conservation until the point when necessary: crack occurrence and consequently the necessity to seal/heal it, when humidity conditions are also ensured (see Figure 6).

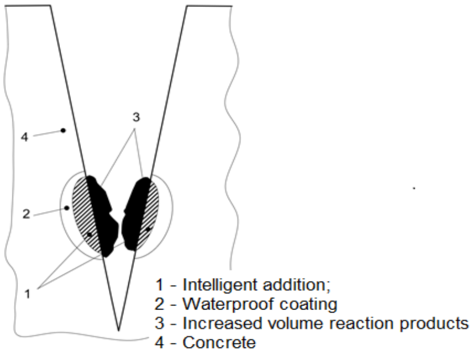

Fig. 6. Graphical representation of the theoretical design for the reactive grains concept

Further on, the preliminary results concerning the practical development of the research concept are going to be briefly presented: the evaluation of potential materials which could be considered proper as reactive grain for the addition, developing and evaluating testing the encapsulation techniques with satisfactory impermeability results with respect to the initial hydration, the capsule compatibility to the cementitious matrix and also the potential healing effect when crack inducing.

4.2. The reactive grains (RG)

Identification of proper reactive grains with suitable characteristics for optimum results represents an important step for the current research. Several aspects are taken into consideration. *The material type*: clinker, alumina cement, blast furnace slag as grinded cement-type material, active hydraulic materials, lime, etc. might comply with the specific requests as reactive grain of the addition, namely to be capable to create new hydration, healing compounds, by reaction with the water or specific ions dissolved therein. They should not contain or generate sulphates, chlorides, alkalis or other aggressive concrete ions, compromising the concrete mass. In the same time, it should not interfere negatively to the hydration or hardening processes naturally occurring to the mix design, in case of accidental capsule braking during the mixing sequences, for instance. The initial experimental procedures are performed by using reactive, 0.09-0.16 mm large, clinker grains.

The physical characteristics are also important for the overall compatibility to the matrix: RG particle dimensions, their content with respect to the whole mass of the PC-RG smart addition and also the dosage of the PC-RG addition to be used in the cementitious composite mix design, with respect to its total mass, for increasing the procedure efficiency without affecting the basic characteristic of concrete or mortar.

4.3. The polymeric coating (PC) for the reactive grains (RG)

The polymeric coating (PC) must be waterproof, protecting the reactive grains from direct contact with water, for preserving their reactive potential until is necessary, namely the occurrence of crack. In the same time, it needs to be strong enough to resist without mechanical damage to initial stresses, like mixing sequences, it has to be stable in the alkaline environment specific to cement based materials and neutral with respect to the initial hydration of the binder, with no interference to this chemical process. Still, it has to develop a brittle behavior along time, so it would be capable to break during cracking process and allow water to react with its core, for the development of further hydration products with crack sealing effect. Economically, the reactive grains (RG) and the polymeric coating (PC) as well prove themselves available in large quantities and adequate for use in the specific concrete making technological processes, so they could easier convince their functionality to the industry, characterized by a conservatory behavior in front of novelty. Regular polystyrene, soluble in ordinary solvents and with a quite low melting point, generally complying with the previous described features, was considered as the coating choice, in two distinct approaches:

Method 1: Mixing the reactive clinker grains (H) with the polystyrene (P) dissolved in compatible solvent, considering as varying parameters the P solution concentration and also the H/P ratios;

Method 2: Mixing the reactive clinker grains (H) with melted polystyrene (see Figure 7).

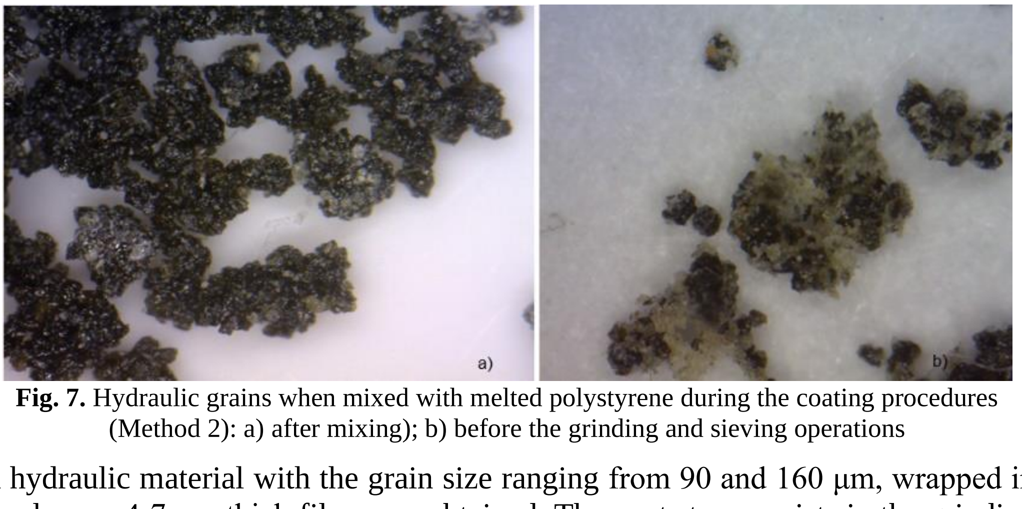

Fig. 7. Hydraulic grains when mixed with melted polystyrene during the coating procedures (Method 2): a) after mixing); b) before the grinding and sieving operations

A hydraulic material with the grain size ranging from 90 and 160 μm, wrapped in a polymer, 4-7 μm thick film, was obtained. The next step consists in the grinding of the mix in order to alter the shells to grain bond granules and then, the sieving through the 0.5 mm sieve, considered to provide the proper dimensions of the final coated grains. These processes lead to partial coating alteration by unavoidably removing a part of the polymeric cover.

The determination of coating waterproofing efficiency is performed by conductivity method, relying the chemical principle that the reaction rate in a heterogeneous system is depending on the contact surface between the two phases, the solid one and the liquid one. The conductivity of the distilled water is measured, containing an amount of reactive addition / protected reactive addition. The decrease of conductivity actually represents the coating efficiency, expressed as a percentage (with respect to the reactive material conductivity). The first 60 s after mixing the distilled water with the reactive clinker grains (virgin and coated) are relevant regarding the conductivity transformation, so this interval is considered relevant for data acquisition.

The Degree of coating (GA, %) was determined by using equation (1):

$$GA\ (\%) = 100 \times \frac{Cond_{hp} - Cond_h}{Cond_h} \tag{1}$$

where: GA (%) = Degree of coating; $Cond_{hp}$ = conductivity of the coated grains suspension; $Cond_h$ = conductivity of the uncoated grains suspension.

4.4. The intelligent addition (PC-RG) compatibility to the cementitious matrix

The compatibility of the smart addition (PC-RG) to the cementitious matrix is evaluated by the means of mechanical performance analysis of mortar specimens. The mixing was performed in accordance to EN 196-1 [14]. The reference sample (R) was produced containing a small amount of polypropylene fibers, also included in the PC-RG mixes. CEM I 52.5R was used as binder, for gaining fast full hydration and also increased consumption of the reactive grain potential and substantial reduction of the self-healing potential, provided via the continuous hydration chemical process. This approach would lead to a better underline of the actual effect of the PC-RG in the mortar, with respect to the reference (R).

The PC-RG addition was provided to the mortar samples as sand replacement (the 0/0.5 mm fraction was considered as partial replacement), as follows: Mixes 130P40 – 130 kg/m^3 PC-RG (by Method 1), Mix 260P40 -260 kg/m^3 PC-RG (by Method 1); Mix 225PT - 225 kg/m^3 PC-RG (by Method 2).

The flexural (3 Point Bending) and compressive characteristics of the mixes were evaluated at the relevant age of 28 days using specific, 40 x 40 x 160 mm^3 prismatic specimens.

5. Results and discussions

5.1. The conductivity testing

The conductivity results proof a reliable efficiency of the PC-RG addition, developed by the means of both methods, Method 1 (Polymer solution) and also by Method 2 (Melted Polymer). Seven from the eleven tested compositions show an efficiency of coverage exceeding 80%, four of them approaching even 90%.

Table 1) Degree of coating for relevant compositions of PC-RG

Method	*Composition code*	*Solution concentration (%)*	*GA (%)*
Method 1 (Polystyrene Solution)	2	2	83
	4	4	85
	6	6	88
	8	8	89
	20	20	88
	30	30	85
	5	10	79
	10	10	66
	15	10	71
	20	10	70
Method 2	(Melted Polystyrene)	-	87

The conductivity development over time, for the reactive grains, without coating vs. a) the coated grains (Method 1) and b) the coated grains (Method 2) is presented in the graphs below (see Figure 8).

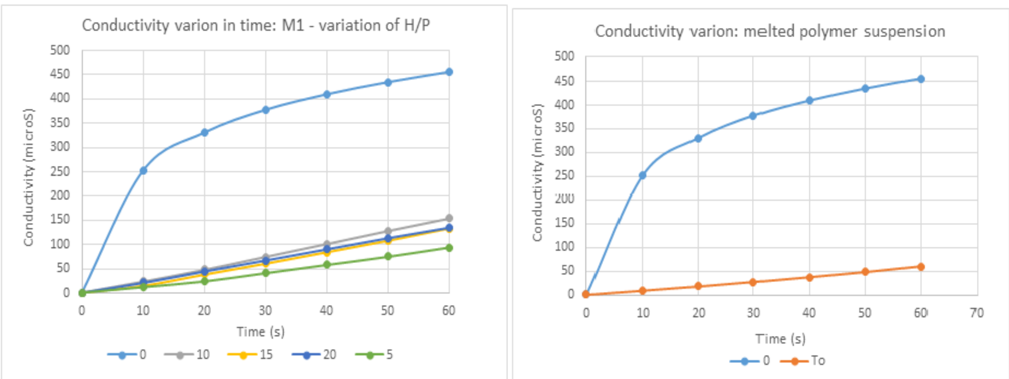

Fig. 8. Graphical variation of the conductivity over time: uncoated vs. coated grains

5.2. The mechanical performance of PC-RG vs Reference mortars

The mechanical performances (3PB flexural and compressive strength at 28 days) of the mortars, with PC-RG addition vs. Reference (R) clearly prove the PC-RG type addition compatibility with the cementitious matrix, not interfering with the chemical processes, like cement grain hydration and hardening. The slight strength increase for PC-RG specimens was associated to the hydraulic active material, available from the remaining uncovered area.

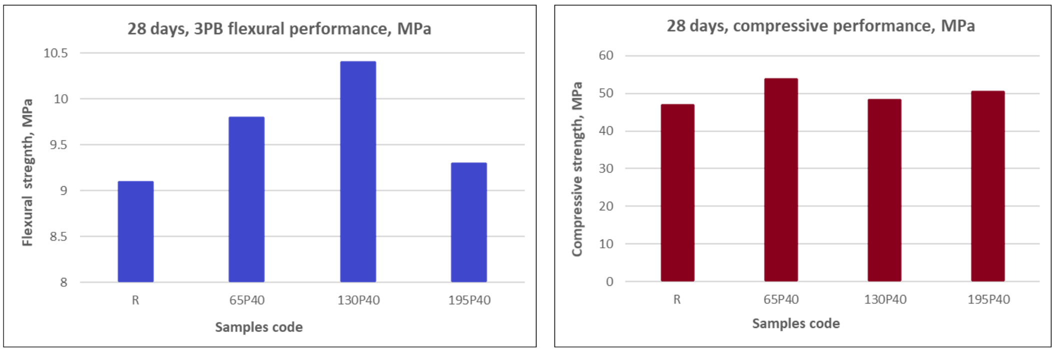

Fig. 9. 28 days 3PB flexural and compressive strength for R and PC-RG specimens

5.3. The self-healing evaluation of the mortar enriched with PC-RG

The self-healing evaluation is performed initially by visual analyses. SEM captures coupled with EDAX (see Figure 10) reveal CSH products near the broken shell of the coating, both inside and outside the capsule. The inside hydraulic active material, is initiating the hydration, developing new hydration, healing compounds, especially hexagonal crystals of $Ca(OH)_2$.

The healing effect is visible when the damage is induced in the cement-based material and the cracking plan intersects the polymeric shell in a proper angle, producing its rupture and consequently initiating the further hydration of the reactive grain inside the shell, now exposed to direct contact to water. At the edge of the crack intact coating can be noticed, further protection of the grain.

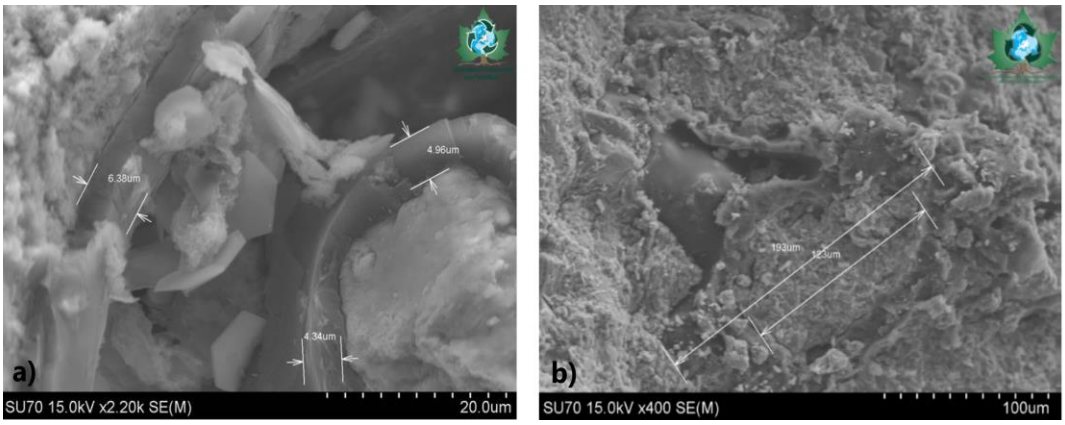

Fig. 10. SEM Capture: Evaluation of the healing degree

Conclusions

The preliminary testing and the obtained results prove the viability of the theoretical concept. The first conclusions are encouraging regarding the aim of the study at this stage. *The reactive grains (RG)* with suitable characteristics were identified and confirmed as suitable for typical cement-based materials: reactive clinker grains, with particle diameter not exceeding 160 micrometers. Supplementary, the RG content must be at least 80% of the total PC-RG addition. The dosage of PC-RG smart addition should range from 5 to maximum 10%, with respect to the total mass of the cement-based material (1).

The polymeric coating (PC): The encapsulation of the RG with a 4 - 7 μm thick polymer film is obtained by immersing them in polystyrene solution/melt, representing a maximum of 20% of the total mass of the addition with self-repair properties. The two methods (Method 1 – Dissolved polystyrene; Method 2 – Melted polystyrene) used as RG encapsulation techniques; show good waterproof performance via conductivity tests (2).

The compatibility of the PC-RG addition to the cement-based matrix was tested via mechanical performance evaluation, PC-RG specimens evaluated with respect to the reference specimens (R), with no addition; the 28 days, 3PB tensile and compressive strength showed slight increase of the PC-RG samples vs. R, attribute to the reactive grains becoming active during mixing (3).

The self-repairing effect of the PC-RG intelligent addition is initially evaluated by electron microscopy analysis, highlighting the presence of a polymeric layer on the surface of the reactive addition. When microcracking is induced within the cementitious matrix the polymeric shell is partially damaged. In the presence of intergranular solution, its diffusion at the polymer film / reactive addition interface is initiated, followed by the initiation of hydration-hydrolysis processes, leading to the formation of additional hydration products, crystallizing in the microcracks in the matrix, healing the area (4).

Further optimization procedures regarding the PC-RG smart addition and adjacent validation of the overall performance of *Cement-based matrix material with self-repair capacity* (Cementitious composites containing the PC-RG addition) represent current stages of the study (5).

Acknowledgment

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