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Synthesis and characterization of silica hybrid materials applicable for defect remediation of concrete

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Application of silica hybrids in concrete field, in particular remediation of the defects is a new area for these materials. It is well known that the concrete variety is the most used and also threatened by destruction material. Formation of defects during the exploitation period is a normal process and remediation via materials, which can block the defects, is the optimal way for preventing their further distribution.

In the present work silica hybrid materials applicable for defect remediation of concrete were synthesized via sol-gel technique. Inorganic network obtained via transformation from liquid to dense material after drying was obtained via tetraethyl orthosilicate. Flexibility and reactivity of silica network is achieved by addition of two organic monomers, known as biocompatible and high reactive – chitosan and polyethylene glycol. After preparation of inorganic – organic solution in a different ratio, $CaCl_2$, as a source of calcium ions were added. The structural results presented formation of amorphous, smooth, high reactive structures. The important factor for application of the hybrid is surface microstructure, as the results showed formation of homogeneous surface on which particles (5 nm – 1 μm) are evenly distributed. Particle size and improvement of the roughness increase with increasing the organic components value.

Compatibility and possibility of prepared hybrids to form $CaCO_3$ was investigated by immobilization of bacterial cells, which synthesized enzyme urease. The biocompatibility and favorable effect of the obtained materials showed, that they can be used for defect remediation of concrete and the treatment can prevent the destruction for a long period.

Key words: Silica hybrid materials, bacterial cells, concrete remediation.

INTRODUCTION

Concrete materials are one of the most used and distributed materials, which are characterized with high resistance, stability and long term durability. During their exploitation period formation of micro cracks is a normal process. During their exploitation period formation of micro cracks is a normal process, as their size increase and can lead to gradually destruction of concrete [1]. The prevention of destruction via chemical way can successfully reduce distribution and growth of the cracks and extend the workability of concrete materials [2]. This type of concrete is called self – healing concrete, as their development and optimization represent interest for many researcher groups [3]. Generally, self – healing effect of concrete implemented by formation of $CaCO_3$ and $Ca(OH)_2$ or after second hydration of unreacted cement on the place of formed cracks. Unfortunately, the mentioned processes are less achievable, for example the second hydration of cement particles is possible for concrete materials up to 7 days after their formation [4]. These problems can be overcome via using of innovative materials, which exhibit self – healing property. They can be added in the concrete mixture or applied as coating for external treatment of micro cracks. Mineral additives, hollow fibers/tubes, microcapsules and living cells are proven as potential self – healing agents [5, 6].

Sahmaran et al. [7] investigated the self – healing effect of three mineral mixtures, based on fly ash with low and high concentration of calcium as well as slag. The permeability of chlorine ions in the structure of concrete samples is investigated and it is established, that low permeability exhibit the sample with slag, as mineral additive. This is

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due to the chemical composition of the slag, as well as small size of the particles [8]. The authors also established that prepared self – healing concrete showed improve properties in moist media. The disadvantage of these self – healing materials is connected with formation of dense structures, which do not prevent formation of cracks and their further distribution [9].

Another opportunity for obtaining self – healing concrete is addition of hollow fibers/tubes in the volume, as their remediation ability is due to material, which is inside [10]. After formation of crack, these materials are released from the fiber/tube and filled the crack. Kim et al. [11] investigated the self – healing effect on concrete cracks using ceramic and glass fibers filled with two type's polyurethane. The polyurethane is chosen, because of its low viscosity and ability to shrink after polymerization. Based on the obtained experimental results the authors established that the ceramic fibers exhibit higher efficiency than glass ones. The efficiency of polyurethane as crack filler depends of position of fibers. The development of correct position of fibers/tubes in concrete sample plays unfavorable effect on their potential application [12].

One of the effective methods for defect remediation of concrete is incorporation of bacterial cells [13]. The compatible cells for that purpose are these, which synthesized enzyme urease, which can provide formation of calcium carbonate [14]. The mechanism of $CaCO_3$ formation is connected with enzyme hydrolysis of urea, as a result of which NH_4 and CO_3 ions are obtained. As a result of high pH and presence of calcium ions, they can easily interact with CO_3 units and formed calcium carbonate as a precipitate. Sources of calcium ions can be organic components and salts. Calcium lactate is a salt, which exhibit good compatibility with bacterial cells and favor further formation of $CaCO_3$. Furthermore, it is established that incorporation of calcium lactate and bacterial cells do not reduce mechanical stability of concrete. The limitation of this type self – healing method is correlated with low stress resistance of the cells and alkali media. Jonckers et al. [15] used for that purpose bacterial cells which exhibit high alkali resistance. Based on the obtained results this researcher group established, that the enzyme activity of cells is kept up to 7 days after addition in the concrete mixture in combination with calcium lactate. After this period the biological activity is slightly reduced, because of the reduce pore size in the concrete sample. Wiktor et al. [16] also investigated the self – healing effect of bacterial cells *Bacilicus alkalinitrilicus* and calcium lactate, as they import them in clay particles for cell protection. The clay particles are chosen, because of their ability to expand after addition in concrete mixture, as this behavior ensures the maintenance of contact surface area for the cells. After preparation of self – healing concrete, the samples are crushed and dipped in water at ambient conditions. After 100 days, the authors established that the formed cracks are filled with white material. The analysis of formed material showed that it is based on calcium, oxygen and carbon, which proved the success formation of $CaCO_3$.

For remediation of concrete via self – healing process is possible via development of material, containing bacterial cells and used as (and applied as) external treatment agent. Mink et al. [17] observed the self – healing effect of solution applied on the surface of concrete samples. The solution contains bacterial cells and calcium salt, which favor formation of calcium carbonate. The experimental results established the optimal quantity of initial components for self – healing of concrete. The used solution easy penetrates in the concrete volume, as a result of which it functionality is reduced. The reduce activity of bacterial cells play unfavorable effect on potential application of this solution. The problem can be solved as development of material, in the role of carrier for bacterial cells. Also in the structure it should contain calcium ions for facilitated formation of calcium carbonate.

Wang et al. [18] treat the concrete cracks with a mixture of silica gel and bacterial cells. The self – healing mixture based on silica sol and bacteria suspension (bacterial cells and NaCl) is poured on the crack place. After transformation of silica sol in a dense material, due to condensation and drying process, the treat concrete sample is immersed in a water solution of urea and calcium ions. The result from the test showed, that the crack is filled with calcium carbonate. Furthermore, it is established that the treat concrete sample exhibit better water resistance than untreated one. The disadvantages of silica materials are connected with their reduce reactivity, as well as reduce reactivity and free surface area during the condensation and drying process, which play unfavorable effect on the efficiency of bacterial cells.

Hybrid materials based on silica, which exhibit affinity to bacterial cells, synthesized enzyme urease are good candidate for development of agent for remediation of concrete defects. The silica component guarantees the stability and durability of self – healing material [19]. Furthermore, this type of materials can easily formed strong interactions with concrete after application. On the other hand, the organic components, which are used, should exhibit affinity to bacterial cells and improve their enzyme activity [20]. The enzyme activity depends of organic biocompatibility, as the cell affinity to the hybrid structure is determined by organic reactivity.

Chitosan is organic component, which exhibit favorable effect to different living cells. The broad application of this polysaccharide is due to free reactive amino and hydroxyl groups, which contains. In acidic media the amino groups can be easily transformed in positive groups, which can form strong interactions with negative biological cells. On the other hand hydroxyl groups can interact with positive cells [21, 22]. Combination of chitosan and silica in one hybrid material lead to formation of structures which are applicable in different fields, where the biotechnology play important role – pharmacy, medicine, food industry, environmental safety and others. This type of hybrid materials are characterized with improve biocompatibility, stability and reactivity [23, 24].

For improving the quantity of reactive centers for possible contact and interaction of hybrid material and bacterial cells combination of chitosan with another organic component is preferred. Polyethylene glycol is synthetic organic component, which can be used for that purpose, because of its biocompatibility, non toxicity and reactivity. This type of material is applicable in different fields from medicine, biotechnology and food industry to technical industry [25]. Tanuma et al. [26] investigated the properties of materials on the based on cross linked polyethylene glycol and chitosan. From the obtained results the authors established that these materials change their structure with pH variation – they expand or reduce the volume if the pH is below 7 the crosslinked organic chains expand, due to specific behavior of chitosan, and opposite situation is observed if the pH is higher than 7.

On the other hand the addition of polyethylene glycol improves the reactivity and hydrophilicity of the hybrid structure due to hydroxyl end groups. The authors also investigated the influence of molecular weight of PEG and established that the mentioned properties are reduced with increasing molecular weight.

The aims of the present study are synthesis, structural characterization and biological application of silica hybrid materials with participation of chitosan and polyethylene glycol, applicable as carrier for bacterial cells and further application for remediation of concrete defects.

EXPERIMENTAL

Synthesis

The silica hybrid materials applicable for external treatment of concrete defects are synthesized via sol-gel technique at ambient conditions, as initial components are used: tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich), chitosan (CS, DD – 75%, Fluka), acetic acid (99.8%, Valerus), polyethylene glycol (PEG, MW 400, Valerus), calcium chloride ($CaCl_2$, 98% Valerus), buffer solution (FICSAL, pH = 7, containing $Na_2HPO_4.2H_2O–KH_2PO_4$, HISTM), hydrochloric acid (HCl, 37%, Merck), distilled water (dH_2O).

The first stage of synthesis is connected with hydrolysis of TEOS using dH_2O and HCl, as initiator of process, as the ratio of these three components is TEOS/ dH_2O/ HCl = 1/0.4/0.4. The organic component CS is previously dissolved in acetic acid solution for better distribution in the silica matrix. After fully dissolution of CS, calculate amount is mixed with the other organic component PEG. Calcium chloride is also previously dissolved in dH_2O, as the ratio is $H_2O/CaCl_2$ = 1/0.1125.

Second stage of synthesis is correlated with mixing of silica sol and organic components, as for preparation of homogeneous structures the hybrid solution is stirred for 30 min via magnetic stirrer. After that the solution of calcium ions with concentration 0.25 g/ml, as well as buffer solution are added for development of mixture compatible for immobilization of bacterial cells. It is established, that the buffer solution led to increasing of pH from 2 to 5. Obtained hybrid mixtures are dried at room temperature in Petri dishes. For establishment of the influence of nature and quantity of organic components the inorganic/organic ratio is varied as follows:

- TEOS/buffer solution = 1/1 (SiCa)
- TEOS/CS/PEG/buffer solution = 1/0.056/0.056/1.11 (SiCSPCa1)
- TEOS/CS/PEG/buffer solution = 1/0.214/0.214/1.43 (SiCSPCa3)

Structural Characterization

The structural characterization is made using four different methods for analysis: X-ray diffraction (XRD, Brucker D8 Advance, CuKα radiation with scan rate of 0.02°.min^{-1} in 2θ range between 10 and 80°), Forier Transforming InfraRed spectrometer (FTIR, MATSON 7000, KBr pellet's, scanning range 300–400 cm^{-1}), Scanning Electron Microscopy (SEM, Philips 515) and Atomic Force Microscopy (AFM, Nano Scope Tapping Mode TM). The pH of hybrid solutions is measured via pH meter (Scott, handylab pH 11/SET, Germany).

Biological test

Application of synthesized silica hybrid materials for concrete remediation is investigated via immobilization of bacterial cells *Bacillus sphaericus*. The used cells produced enzyme urease, which favors formation of calcium carbonate. The hybrid materials are dipped in bacterial suspension for achievement of immobilization process. After that obtained system material (as a carrier) with the bacterial cells are putted in a urea solution for initiating formation of $CaCO_3$. For establishment of compatibility of obtained hybrid materials, the biological activity of cells, which are immobilized, is measured.

RESULTS AND DISCUSSION

The FTIR spectra (Fig. 1) showed characteristic peaks of silica network formed via sol-gel technique at room temperature, in the role of backbone inorganic component of hybrids (Si-O-Si asymmetric and symmetric vibrations – 1080 and 450, 560, 790 cm^{-1};

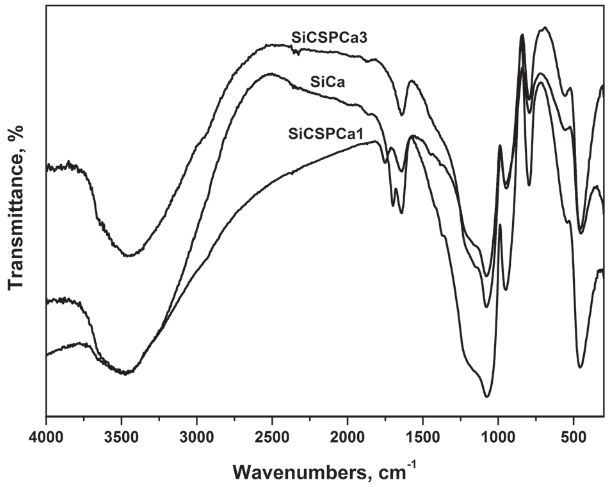

Fig. 1. FTIR spectra of obtained silica hybrid materials

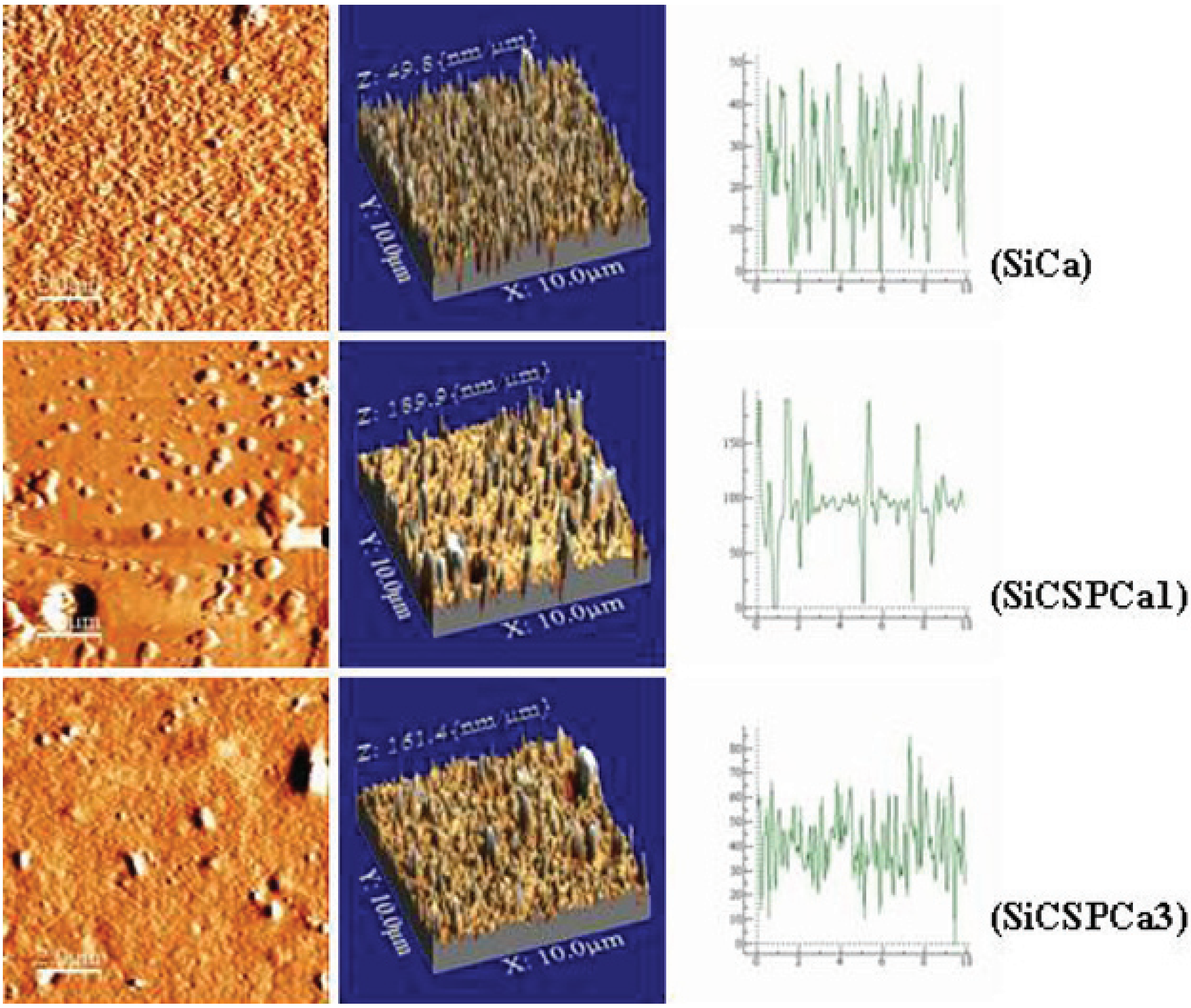

Fig. 2. AFM 2d, 3d topography and roughness profile of obtained hybrid materials

Si-OH – 950 cm^{-1}, Si-O-C – 1000–1200 cm^{-1}, H-OH – 1640 and 3400 cm^{-1}) [27].

The wide range peak around 1100 cm^{-1} is also corresponding to C-C structural units of CS and PEG. The existence of hydroxyl and amino peaks, which play important role for interaction with bacterial cells and incorporate in the hybrid structure due to used organic components are associted with the peaks at 950, 1640 and 3400 cm^{-1} [28].

The surface microstructure is investigated via AFM analysis, because it plays important role for contact area of cells (Fig. 2). The 2d and 3d images of sample SiCa showed formation of rough surface, as the z-coordinate is 49.5nm.µm. The third micrograph, which presented roughness profile, showed formation of particles, which are closely relative to each other. The dense distributions of the particles lead to limitation of contact surface area for bacterial cells.

The results for sample SiCSPCa1 showed formation of homogeneous silica network into which the particles are evenly distributed. The successful preparation of ordered, amorphous hybrid structures, established from AFM results is confirmed via obtained XRD patterns. The z-coordinate increase up to 159.9nm.µm, and the distribution profile showed improvement of contact surface area. Optimal results for roughness and contact surface area presented sample SiCSPCa3.

The possibility of obtained hybrid materials to be applied as self – healing agents for concrete defects is connected with compatibility of them with bacterial cells, synthesized enzyme urease, as well as further formation of calcium carbonate. Model schema of obtained hybrid structure, based on obtained FTIR spectra, showed successful formation of silica network, distribution of CS, PEG and calcium ions in it. The possible reactive centers, reactive groups on cell walls, as well as their potential interaction are also presented on the Figure 3.

The biocompatibility is established via measurement of biological activity of immobilized cells. The obtained results, which presented the activity for a period of time are shown on Figure 4. The activity is measured every 12 h. The result for sample SiCa showed, that the Initial activity of immobilized

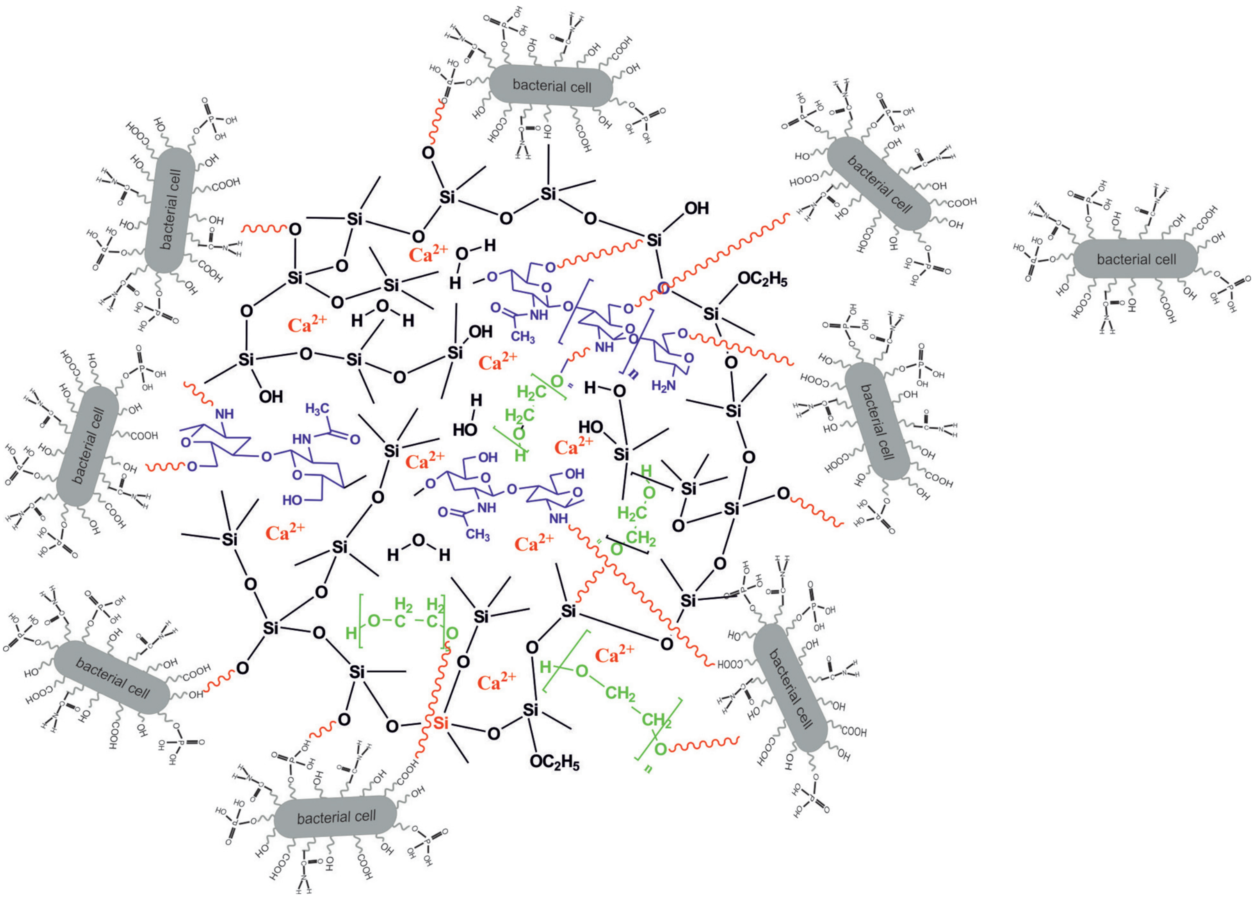

Fig. 3. Model schema of potential interaction between reactive groups of hybrid material and bacterial cells

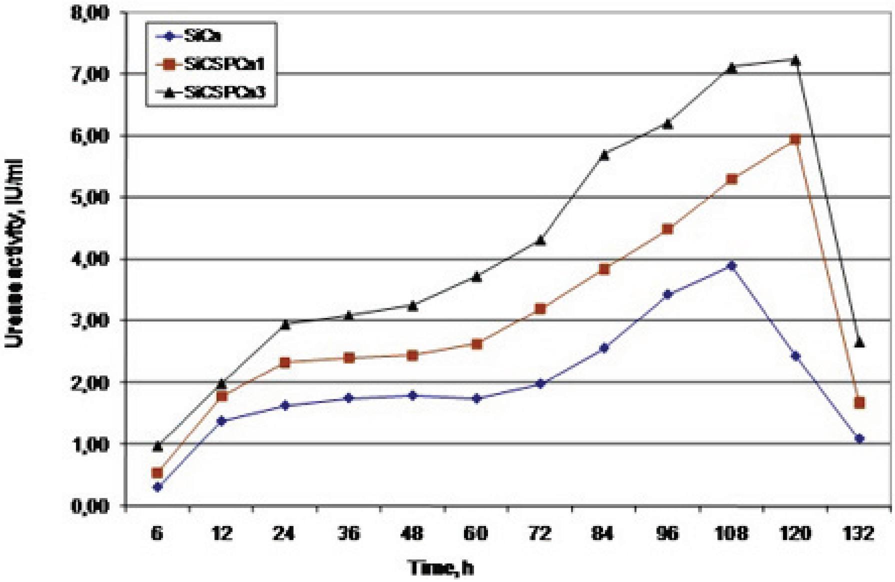

Fig. 4. Urease activity of immobilized bacterial cells to obtained silica hybrid materials

bacterial cells is below 1IU/ml, after which slightly increase up to 3.9 IU/ml on the 102 h.

With addition of CS and PEG, the urease activity increase, as on 112 h reached to 5.9 IU/ml. The higher values are due to improve reactive and contact centers of silica structure. These results showed the favorable effect of used organic components to bacterial cells. Highest value of bacterial activity presented hybrids with composition SiCSPCa3 (7.2 IU/ml on 112h). The enzyme activity result for the third sample showed, that this hybrid structure exhibits improve functionality and reactivity. The evenly distribution of organic particles (established from AFM analysis) led to improve contact surface area with the bacterial cells. Furthermore, it is proven that, the used inorganic/organic ratio ensure compatibility and favorable effect on the long efficiency of the cells.

Based on the obtained results for enzyme activity, the surface of sample SiCSPCa3 after biological cells is investigated via SEM analysis.

The micrograph (Fig. 5) showed existence of crystal particles. The formation of these particles showed successful formation of a product after interaction of hybrid material and bacterial cells in the presence of urea solution, which can be associated with calcium carbonate, as bioprecipitate. Based on this result can be concluded, that obtained hybrid materials in combination with bacterial cells can be applied for self – healing agents for concrete, which can filled the cracks with bio calcium carbonate.

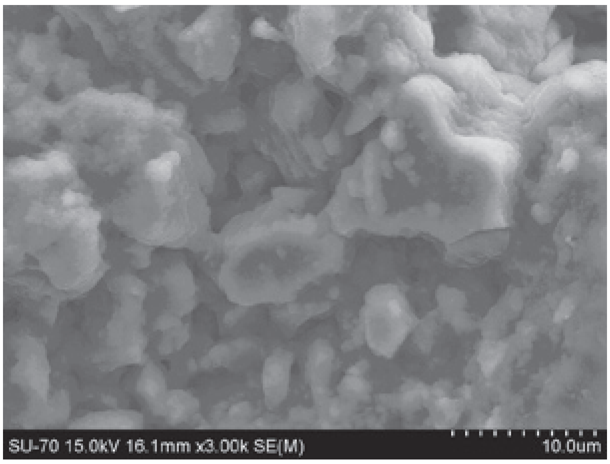

Fig. 5. SEM micrograph of SiCSPCa3 surface after immobilization with bacterial cells and immersion of urea after 24 h

CONCLUSION

Silica hybrid materials with participation of CS and PEG applicable for self – healing of concrete defects are synthesized by sol-gel method. The results from structural characterization showed, that obtained hybrids are amorphous, homogeneous and reactive structures. The results from biological test proved their biocompatibility and favorable effect on enzyme activity of immobilized calls. The SEM micrograph for the sample with higher quantity CS and PEG (SiCSPCa3) showed formation of crystals on the surface, which can be correlated to bio calcium carbonate. The investigations proved that the synthesized silica hybrid materials can be applied as self – healing agents for concrete.

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СИНТЕЗ И ОХАРАКТЕРИЗИРАНЕ НА СИЛИКАТНИ ХИБРИДНИ МАТЕРИАЛИ, ПРИЛОЖИМИ ЗА ОТСТРАНЯВАНЕ НА БЕТОННИ ДЕФЕКТИ

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(Резюме)

Приложението на силикатните хибриди в областта на бетоните и в частност отстраняване на дефектите им е нова сфера за тези материали. Известно е, че бетонните изделия са едни от най-използваните и предразположени на разрушаване материали. Формирането на дефекти по време на експлоатационния им период е нормален процес, като отстраняването им чрез материали, които могат да блокират дефектите, е оптималният подход за предотвратяване на тяхното последващо разрушаване.

Настоящата работа е свързана със синтез на силикатни хибридни материали, приложими за отстраняване на дефекти на бетонни изделия посредством зол-гелната технология. Неорганичната матрица, получена чрез трансформирането на течност в плътен материал след сушене, е синтезирана посредством тетраетил ортосиликат. Пластичността и реактивоспособността на силикатната матрица е подобрена чрез добавянето на два органични мономера, известни като биосъвместими и реактивоспособни – хитозан и полиетилен гликол. След получаването на неорганично-органичният разтвор в различни съотношения, е добавен $CaCl_2$, като източник на калциеви йони. Структурните изследвания показват формирането на аморфни, гладки и реактивоспособни структури. Важен фактор за приложимостта на хибридите е повърхностната микроструктура, като резултатите показват формирането на хомогенна повърхност, на която равномерно са разпределени частици (5 nm – 1 μm). С повишаване на количеството органичен компонент се наблюдава нарастване на размера на частиците, както и подобряване на грапавостта.

Съвместимостта и възможността на получените хибриди да формират $CaCO_3$ е изследвана чрез имобилизиране на бактериални клетки, които синтезират ензим уреаза. Биосъвместимостта и благоприятният ефект на получените материали показват, че те могат да бъдат използвани за отстраняване на дефекти на бетонни изделия и обработката може да предотврати разрушаването им за дълъг период от време.