SOL - GEL SILICA HYBRID MATERIALS APPLICABLE FOR EXTERNAL TREATMENT OF CONCRETE DEFECTS

Elena Todorova, Georgi Chernev, Stoyan Djambazov, Yana Tsvetkova

ABSTRACT

The sol-gel silica hybrids are materials with application in different fields - pharmacy, medicine, sensors, etc. Concrete self-healing is a new area of applications of this kind of materials. It is connected with filling the cracks and preventing their further destruction as well as providing materials able to form CaCO₃ as filler. A combination of hybrid materials containing calcium ions and bacterial cells is the optimal choice for that purpose. The material should exhibit stability, durability and ability to penetrate in the cracks. Furthermore, it should be reactive and biocompatible in order to interact with bacterial cells and promote further formation of CaCO₃.

Hybrid materials based on silica network and in situ incorporated organic components (chitosan and polyethylene glycol) is synthesized by the sol-gel method. The silica matrix obtained from tetraethylorthosilicate provides the structure with stability and durability, while the organic components account for its flexibility, biocompatibility and reactivity. The results from the structural analysis (XRD, FTIR, SEM and AFM) show that hybrids thus obtained have an amorphous, homogeneous structure. Formation of the silica network and backbone organic units is observed by FTIR spectroscopy. The AFM surface micrographs show the presence of particles of a size from 50 nm to 1 μm. They serve as reactive centers for potential interactions with the bacterial cells. The results from the structural characterization show that the synthesized materials can be used as carriers for bacterial cells’ immobilization and applied further as fillers for external treatment of concrete defects.

Keywords: sol-gel, silica hybrids, nanomaterials, concrete defects.

INTRODUCTION

Silica hybrid materials produced by the sol-gel technique are of great interest in different fields - medicine, pharmacy, biocatalysis and bioreactors, electronics, solar cells and fuel cell membranes [1 - 6]. The silica plays an important role in the stability and reusability of the hybrid materials [7]. The organic components are chosen according to the desired structural characteristics and properties with respect to their application [8, 9]. The sol-gel process is an accessible preparation method which allows modifications dictated by the specific requirements referring to the structure of the hybrid variety [10]. Silica hybrids in combination with biological cells form biosystems are applied as drug delivery systems as well as for biodegradation and biosorption of environmental contaminants [11 - 15].

Another area for application of silica biohybrids is self-healing of concrete products [16]. The self-healing materials should repair the concrete defects formed during the exploitation period [17]. It is well-known that formation of calcium carbonate at the site of a concrete crack is the optimal way of remediation. The combination of hybrid materials with bacterial cells synthesizing the enzyme “urease” and calcium ions [18] is a suitable treatment. The crucial factor for the success of the self-healing process is the biological activity of the living cells. Immobilization in suitable carriers can prolong this ability [19]. The carriers should exhibit stability, flexibility and durability when used as crack fillers. On the other hand, they should be highly reactive and biocompatible in order to provide interactions with bacterial cells.
silica hybrid materials are promising candidates because they are readily produced by the sol-gel method. They are stable and durable structures whose interactions and compatibility with bacterial cells depend on the nature of their organic component [20]. B. Pigino et al. [21] investigated the influence of an ethyl silicate based coating on the concrete properties. The experimental results showed that the treated concrete exhibited improved chloride and CO₂ resistance than that of the untreated one. The barrier mechanism of the silica coating applied lead to the improved concrete durability. J. Cox et al. [22] established the existence of amino, hydroxyl, carboxylic, phosphoric and phosphodiester groups on the bacteria surface working as active centers for interaction with other materials and which why it was suggested that the carrier structure should contain functional groups compatible for interaction with bacterial cells [23].

Chitosan (CS) is a natural polymer with high reactivity in respect to different living cells, because of two hydroxyl- and amino end-groups in the polysaccharide structure. Chitosan, in combination with a silica material, produces hybrids with improved biocompatibility, flexibility, reactivity and stability [24]. Good results are achieved in case separate particles of CS are evenly distributed within the silica matrix [25]. Under acidic conditions the amino groups of CS can be easily protonated and converted to soluble groups resulting in the organic component degradation [26, 27]. The combination with another organic component can prevent this effect and protect CS. Polyethylene glycol (PEG) can be considered for that purpose. It is as well characterized by biocompatibility, hydrophilicity, non-toxicity and reactivity because of the free reactive end hydroxyl groups in its structure [28]. Furthermore, PEG improves the mechanical stability of the hybrid structure [29].

Wong et al. [30] investigated the influence of PEG and CS on the weight, degree of swelling and the mechanical properties of alginate microcapsules. It was concluded that the hydroxyl groups of both components attracted water molecules and alginate hydrophilicity was improved. The stability of these end-groups increased resistance of alginate microcapsules in different solutions (pH 3, 7, 10).

Our work focuses on the sol-gel synthesis and structural investigation of silica hybrid materials as carriers for bacterial cells’ immobilization with a view to apply our results to the external treatment of concrete defects.

EXPERIMENTAL

The sol-gel method was used for the synthesis of the silica hybrids under investigation. The following starting materials were used: tetraethyl orthosilicate (TEOS, 98 %, Sigma Aldrich), chitosan (CS, DD - 75 %, Fluka), polyethylene glycol (PEG, MW 400, Valerus), a buffer solution (BS, FICSAFl, pH = 7, Na₃HPO₄·2H₂O·KH₂PO₄, HISTM), acetic acid (99.8 %, Valerus), hydrochloric acid (HCl, 37 %, Merck), distilled water (dH₂O).

The inorganic matrix was prepared by hydrolysis of TEOS in the presence of HCl at a ratio of TEOS: H₂O: HCl equal to 1:0.4:0.4. The reactivity and biocompatibility of the silica material was improved through the incorporation of CS (previously dissolved in 1 % acetic acid) and PEG. Composition ratios used for the preparation are listed in Table 1. The addition of BS (pH 5) is worth noting.

The determination of the hybrid state was performed by X-ray diffraction using a Brucker D8 Advance diffractometer (CuKα radiation with a scan rate of 0.02° min⁻¹ in 2θ range between 10 and 80°). The identification of separate structural groups in the composition of the materials was evaluated by a MATSON 7000 spectrometer (KBr pellets) in the scanning range of 300 cm⁻¹ to 4000 cm⁻¹. The microstructure of the hybrids was characterized by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) using a Philips 515 scanning electron microscope and a Nano Scope Tapping Mode TM atomic force microscope respectively. The pH of the hybrid solution was controlled with a pH meter (Schott, handy lab, pH11/SET, Germany).

RESULTS AND DISCUSSION

Fig. 1 shows the X-Ray diffraction patterns of the materials under investigation. The results obtained reveal the presence of an intensive wide range peak around 23° which corresponds to an amorphous hybrid structure. D. Enescu et al. [31] compared XRD patterns of pure CS and SiO₂-CS hybrid materials and found that crystalline peaks of organic component disappeared in combination with the silica source. Silva et al. [32] who also synthesized hybrid materials based on silica and CS established the existence of one wide halo around 23-20° corresponding to a combination of amorphous inorganic-organic components in one hybrid composites.
The FTIR spectra (Fig. 2) show presence of characteristic peaks of silica matrix obtained using the sol-gel technique under ambient conditions. As a result of hydrolysis-condensation reactions, Si-O-Si backbone units are formed. Their asymmetric and symmetric vibrations are attributed to the peaks at 1080 cm⁻¹, 450 cm⁻¹, 580 cm⁻¹ and 790 cm⁻¹, respectively. Moreover, Si-OH groups-peak is outlined at 950 cm⁻¹, while the broad Si-O-C units peak is recorded between 1000 - 1200 cm⁻¹. The presence of Si-OH and Si-O-C is associated with not fully accomplished hydrolysis of the silica precursor. The presence of H-OH groups (peaks at 1640 cm⁻¹ and 3450 cm⁻¹) in the hybrid compositions is due to the low-temperature synthesis method and the subsequent drying of the materials at room temperature [33, 34].

The peaks at 950 cm⁻¹, 1450 cm⁻¹, 1640 cm⁻¹ and in the range of 3200 cm⁻¹ - 3450 cm⁻¹ overlap with those characteristic for the amino, amide end-groups of CS and hydroxyl groups of CS and PEG, respectively [35]. The main C-C-O structural units of CS and PEG refer to the peak at 1000 cm⁻¹-1200 cm⁻¹ [36]. The peaks at 1383 cm⁻¹ and 1450 cm⁻¹ are associated with vibrations of –CH₂ groups in PEG [37]. The peaks in the range of 2320 cm⁻¹ - 2360 cm⁻¹ are related to Na₂HPO₄ and 2H₂O, KH₂PO₄ from the buffer solution [38].

The FTIR spectra information obtained verifies the successful synthesis of the hybrid structures containing Si-O-Si, CS and PEG characteristic units with the simultaneous preservation of their end functional groups. According to Ling-hao He et al. [39] and F. Mahatmanti [40] who investigated chitosan-PEG and silica-CS-PEG films the absence of new peaks could be associated with intermolecular hydrogen interactions between the components. The microstructure of the prepared hybrid materials is investigated by SEM analysis and the results are shown in Fig. 3. The micrographs prove the formation of a silica matrix based homogeneous structure formed by the sol-gel technique under ambient conditions and its compatibility with the organic components.

The cracks observed for sample SCP3 (micrograph c) are due to the mode of the sample preparation for analysis. Formation of a rough structure and existence of particles and aggregates is observed in case of sample SCP4. This can be associated with interpenetrating and H-bonding between the organic components. On the other hand, the particle formation can result from the lower stability of CS during the solution pH change. Other research groups [41, 42] found that pH increase up to 5 leads to shrinkage of the polyssacharide units and formation of bigger particles.

### Table 1. Composition of the samples under investigation.

<table>
<thead>
<tr>
<th>Sample abbreviation</th>
<th>Ratio TEOS:CS:PEG:BS</th>
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<tbody>
<tr>
<td>SCP1</td>
<td>1:0.056:0.056:1.11</td>
</tr>
<tr>
<td>SCP2</td>
<td>1:0.125:0.125:1.25</td>
</tr>
<tr>
<td>SCP3</td>
<td>1:0.214:0.214:1.43</td>
</tr>
<tr>
<td>SCP4</td>
<td>1:0.333:0.333:1.67</td>
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</table>

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Fig. 3. SEM micrographs of synthesized silica hybrid materials with a different quantity of CS and PEG.

Fig. 4 presents AFM analysis images of the hybrid materials. A homogeneous structure with evenly distributed organic components is been observed in case of sample SCP1. Its particles size is between 50 nm - 150 nm. The roughness profile shows the existence of free sites between the particles which can be associated with the improved contact surface area and the possible interaction between the bacterial cells and the hybrid. Similar 2d and 3d surface characteristics and roughness profile are observed for sample SCP2 for which a larger particle size is found (z-coordinate is 1664 nm/μm). The increased quantities of CS and PEG (sample SCP3) lead to a decrease in the size of the particles (50 nm - 160 nm). The roughness profile shows an even distribution of individual particles which are close to each other. Formation of large particles or aggregates is observed in the sample of the highest amount of CS and PEG (CPS4). This result is in correspondence with the data from the
SEM analysis. The AFM analysis of the samples under investigation shows that the hybrid structures can be used as carriers for bacterial cells.

Kim Tittelboom et al. [43] investigated the self-healing effect of bacteria on concrete as they sprayed directly into the cracks a silica sol (amorphous silicon dioxide) containing the bacteria. The water permeability experiments showed improved resistance than that of the untreated cracked samples. That was due to the penetration of silica sol into the crack and its further transformation to a dense solid material. Furthermore, it was established that the silica gel protected the bacteria from the concrete environment high pH and ensured the formation of calcium carbonate crystals. The research group found that the silica gel could be successfully used as crack filler and bacteria protection material. The silica materials are chemical inert, but limitations as biocompatibility, flexibility and reactivity reduce their potential application.

The combination of silica with CS and PEG provides the development of hybrid materials of improved functionality and biocompatibility.

The results from the structural analysis show that the hybrid materials obtained can be used as carrier for cells immobilization. Furthermore, the addition of calcium ions source (for example CaCl₂) can favor CaCO₃ formation which is the optimal way for treatment of concrete defects.
CONCLUSIONS

Hybrid materials containing inorganic and two organic components are prepared by the sol-gel method of synthesis. The hybrid structures are based on silica networks into which CS and PEG are incorporated and evenly distributed. The prepared materials are amorphous, homogeneous and stable which enables their use as carriers for immobilization of bacterial cells. Further experiments focusing on the biocompatibility and reactivity are planned aiming to obtain materials with a potential application for external treatment of concrete defects.

REFERENCES
