

Sol-gel silica hybrid materials – characterisation and long-term stability

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Main goal of the present work was the synthesis of reactive silica hybrid materials and the investigation of their water stability for a long period of time. For the improvement of silica reactivity, which is the base structural component of these hybrids different types of natural and synthetic organic materials were used – chitosan (CS), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and methacrylic acid (MA). The structural characteristics of the obtained silica hybrids are investigated via XRD and SEM analysis. The XRD data reveals successfully formation of amorphous silica hybrid material. The SEM micrographs show the specific chemical properties of the chosen organic components, play important role on the final hybrid morphology. EDX analysis is used for establishment of the hybrid materials chemical/elemental composition. In order to investigate their long-term stability, the synthesised sol-gel silica hybrids are immersed in a water solution for 48 and 168h. Their weight changes were evaluated. The experimental results of the immersed samples presented high stability for a long period for the specimens from the following compositions-silica/MMA and silica/CS/MMA. The opposite behaviour (low stability) was shown from the silica hybrids with participation of HEMA and combination of CS and HEMA.

Keywords: sol-gel, silica, chitosan, acrylates, water stability.

1. INTRODUCTION

The hybrid materials, based on sol-gel silica, are interesting type of chemical structures, because of their long term stability in different pH media [1]. This property is favoured by the dense inorganic structure, which is formed via hydrolysis and condensation reactions. Other main advantage of these types of silica materials is the easy preparation technique, based on the mixing of liquid precursor, distilled water and acid solution [2, 3].

The application area of sol-gel silica materials can be expanded via modification with organic components and development of innovative hybrid structures with specific properties. There is a variety of organic additives to choose from, depending on the requirements towards the end hybrid material, i.e. long or short organic chain length, one or more end reactive groups, biocompatibility, stability, hydrophilicity and others [4, 5].

Our research group is focused on the development of silica hybrid materials, which can be applied as sorbents for contaminants [6, 7]. For that

purpose, we synthesised silica hybrids with participation of natural (chitosan) and synthetic (methacrylic acid, methyl methacrylate and hydroxyl ethyl methacrylate) organic materials. The chosen organic components are known as biocompatible, reactive materials, which can be successfully applied for the sorption of contaminants [8, 9].

Copello et al. [10] investigated the dye sorption behaviour of chitosan/SiO₂ hybrid materials. Via FTIR and XPS analysis, the authors established that the synthesised hybrids are of crossed linked chain type, i.e. combination between organic and inorganic units, bonded/connected/joined through covalent bonds. This can be used as a proof for the preparation of stable in water media structures. Furthermore, testing the absorption behaviour of the synthesized materials, there was found great attraction ability between the negatively charged end groups of the used organic dyes and positively charged amino end groups of chitosan. Another researcher group [11] investigated the behaviour of silica-chitosan membranes in different media at different pH (varying from 2.5 to 7.5). The silica component is chosen because of its stability in different media, while the chitosan is used for its pH sensitivity. In acid media, the chitosan expands, because of amino group protonation, while in basic media the polysaccharide

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structure, and has the ability to shrink. The test results showed expanding of the hybrid structure for a pH increase from 2.5 to 7.5.

Acrylates are synthetic organic components, which exhibit good compatibility with silica. The combination of SiO₂ and acrylate leads to formation of highly mechanical and thermally stable hybrid structures. On the other hand, the organic components can improve/increase the sorption capacity of silica due to presence of free reactive end groups [12–17].

The combination of chitosan and acrylate should lead to an improved sorption capacity for Cr of the obtained hybrid silica-based material. Tahaet al. [18] synthesised silica hybrid materials with the participation of modified chitosan. As modifier of the natural organic component is used poly butyl acrylate, as the reason is activating chitosan reactivity. The IR analysis showed that the prepared hybrid structures contain –OH and –NH₂/–NH₃ groups. After contact of the synthesized material with chromium ions, the characteristic peaks of reactive centres have been shifted from 3429.43 cm⁻¹ to 3525.88 cm⁻¹, which proved the interaction of the contaminant (Cr) and sorbent. Furthermore, the intensity of Si-OH peak is decreased, which showed that the silica network also takes part in water purification process.

The main goal of the present work is the establishment of the long-term stability in water media of the obtained silica hybrid materials. For synthesis via sol-gel of potential stable hybrid structures different combinations of inorganic (silica) and organic components are used. XRD, SEM and EDX analyses are used for investigations of the correlation between structure and properties.

2. EXPERIMENTAL

2.1. Materials used

Tetraethyl orthosilicate (TEOS, Sigma Aldrich, 98%), chitosan (CS, degree of deacetylation 75–

85%, Fluka), 2-hydroxyethyl methacrylate (HEMA, 97%, Sigma Aldrich), dH₂O, HCl (37%, Fluka), methyl methacrylate (MMA, Fluka), methacrylic acid (MA, Sigma Aldrich) and acetic acid (99%, Sigma Aldrich) were used as initial precursors for the preparation of silica hybrid materials.

2.2. Synthesis procedure

For the synthesis of the silica hybrid materials the following sequence has been used – preparation via sol-gel reactions of silica network, addition of organic components and drying at ambient conditions. The silica matrix is obtained via mixture of TEOS, dH₂O and 1M HCl, as catalyst, in a solution ratio – 1:0.4:0.4. The ratio was kept constant for all samples. Separately 1 g chitosan powder was dissolved into 100 ml 1M acetic acid solution. After full dissolution of chitosan, the calculated amount of organic solution was added to the obtained silanol. The solution was stirred for 30 min and after that the acrylate components were added to the homogeneous sol and the stirring continued for another 30 minutes. The obtained hybrid “sol” was poured onto Petri dishes in order to achieve its transformation into gel. The synthesis scheme of obtained silica hybrid materials is presented on Fig. 1. The ratio of initial components as well as abbreviations of the synthesized hybrid materials are presented in Table 1.

2.3. Methods for characterization

XRD (Bruker D8 Advance; Cu-K α radiation with scan rate of 0.02° min⁻¹ in the 2 θ range between 10 and 80°) was used to determine the phase composition and state (amorphous or crystalline) of the obtained hybrid materials. SEM and EDX spectroscopy (Hitachi SU-70) were used for observation of the surface and volume characteristics of the synthesized hybrid materials. The long-term stability of the synthesized hybrid materials was evaluated via immersion for 48 and 168 h in water solution (pH = 7).

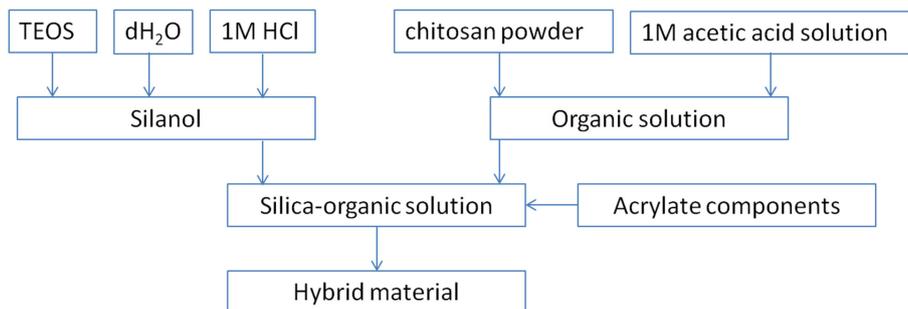


Fig. 1. Synthesis scheme of obtained hybrid materials.

Table 1. Composition ratios used for synthesis of silica hybrid materials

Sample abbreviation	TEOS	H ₂ O	HCl	CS	MA	MMA	HEMA
Pure silica	1	0.4	0.4	–	–	–	–
SiCS5	1	0.4	0.4	1			
SiMA5	1	0.4	0.4		1		
SiMMA5	1	0.4	0.4			1	
SiHEMA5	1	0.4	0.4				1
SiCSMA5	1	0.4	0.4	0.5	0.5		
SiCSMMA5	1	0.4	0.4	0.5		0.5	
SiCSHEMA5	1	0.4	0.4	0.5			0.5

The water stability of the synthesized hybrid materials is investigated via placement of preliminary determined amount of the obtained samples into distilled water. After 48 h and 168 h, the samples are removed from the water and the weight change is measured and the results are shown as % of weight loss in Figs. 2 and 3.

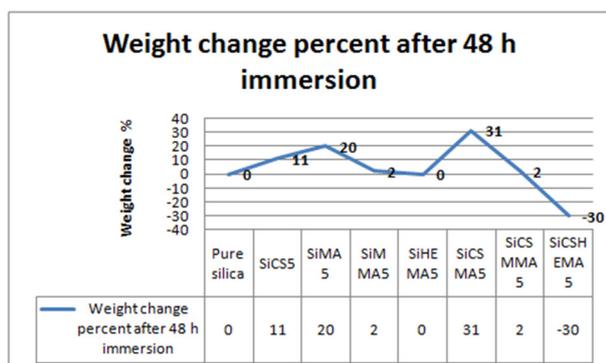


Fig. 2. Weight change in percent for the obtained silica hybrid materials after immersion in water solution for 48 h.

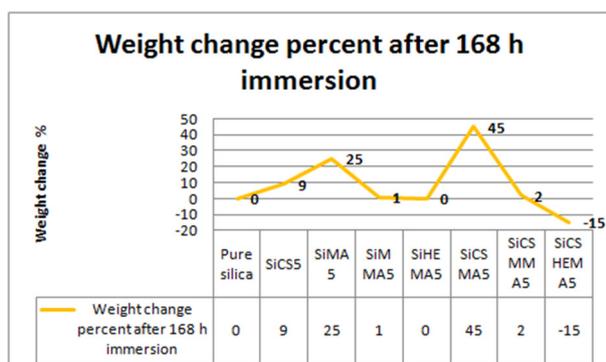


Fig. 3. Weight change [%] of obtained silica hybrid materials after immersion in water solution for 168 h.

3. RESULTS AND DISCUSSION

The main objective of our work is the preparation of reactive hybrid structures, which possess long-term stability in water media. Based on the literature survey, it was established, that the easiest/simplest way to prepare functional structures is to initially obtain silica network and subsequently to add evenly distributed organic units into it. The good compatibility of silica and chitosan, as well as that between silica and acrylates, allows the preparation of stable, monolith materials. On the other hand, the used organic components containing end reactive positively and negatively charged groups, have to be evenly distributed in the silica network. This is a major pre-requisite for ensuring potential application of the hybrid materials as sorbent of different contaminants.

The phase composition of the synthesized hybrid materials is investigated by XRD analysis. All of the obtained structures are amorphous. The presence of halo around 23 2 θ proved successful formation of silica network (Fig. 4).

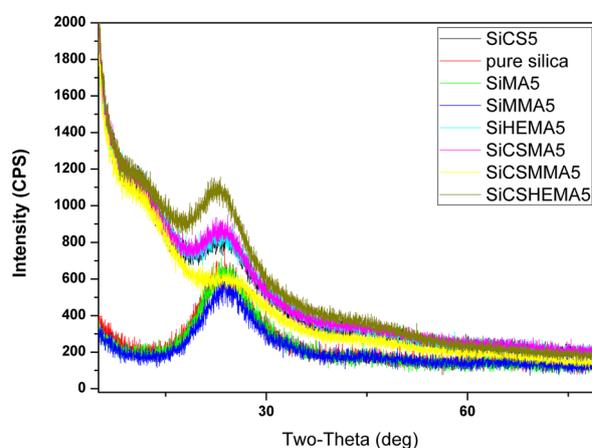


Fig. 4. XRD patterns of the hybrid materials synthesized via sol-gel technique.

The surface morphology characteristics of the synthesized hybrid structures are investigated by SEM (the micrographs are shown in Fig. 5).

The micrograph of the 1st sample presents the smooth, monolith structure of pure silica. Due to the appropriate ratio between the silica precursor, dH₂O

and acid a uniform surface is formed. The 2nd micrograph, corresponding to the silica – chitosan hybrid materials, showed improvement of silica roughness. The small particles, which are evenly distributed all over the surface and with varied sizes, are associated to the added chitosan component.

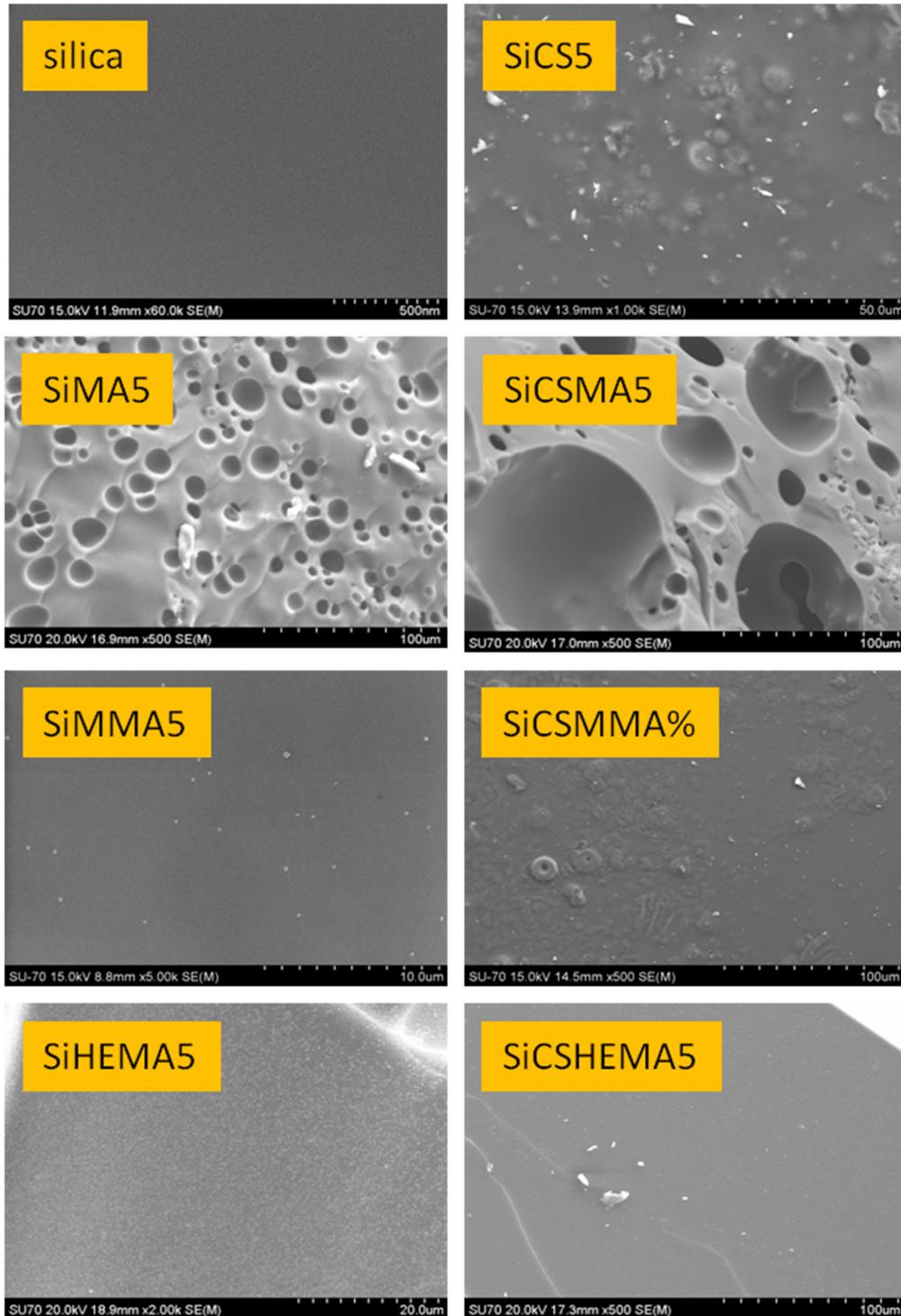


Fig. 5. SEM micrographs of sol-gel synthesized silica hybrid materials.

Significant difference in the obtained microstructure is observed for the combination of silica and MA (Fig. 5 – SiMA5). A lot of pores with equal size are observed all over the hybrid surface. The porosity of the hybrid structure is due to used synthetic component. The presence of pores into the silica network improves the contact surface area with external moieties, e.g. contaminants in the waste water for example.

The combination of silica with MMA and HEMA leads to formation of homogeneous structures (based on sol-gel silica network) showing evenly distributed particles with size between 0.5 and 10 μm .

Some differences in the SEM micrographs of silica hybrids for/in case of combination of natural and synthetic organic components are observed. The combination of CS and MA leads to formation of larger pores all over the hybrid surface (larger than 50 μm).

The addition of MMA to the SiCS hybrid structure led to a decrease of particle sizes and roughness of the surface. The addition of CS to the silica-HEMA structure led to increasing number of particles all over the surface.

The chemical composition of some of the hybrid materials – pure silica, SiMA5 and SiCSMA5 is investigated by EDX analysis (Fig. 6). All of the spectra presented existence of Si, O and C atoms. Differences of percent/ concentration values are observed – the quantity of C and O atoms increased with addition of organic components to the silica network. Existence of C atoms in the structure of the sample corresponding to pure silica (0, 6) is due to used sol-gel synthesis at ambient conditions.

The results from the water stability tests showed, that the pure silica material didn't change its weight during the immersion in water. The combination of silica and chitosan possesses different behavior – the weight increases after immersion for 48 h with 11% and slightly decrease to 9% after 168 h. This behavior can be associated with the property of chitosan component, which expands its units in neutral media. The existence of –OH and amino groups of CS supports the easy interaction and sorption of water molecules onto the respective hybrid materials. There are the silanol units, due to used sol-gel technique, realized at standard conditions that also improve the sorption properties. The SiMA5 material possesses the highest weight loss in percent – 20% at 48 h and 25% at 168 h. This behaviour is due to porosity of the material, which increases the contact surface area between water molecules and reactive hydroxyl groups of MA and silica units. Opposite property/behaviour showed the samples SiCSMA5 and SiCSHEMA5, which slightly/scarcely change their weights.

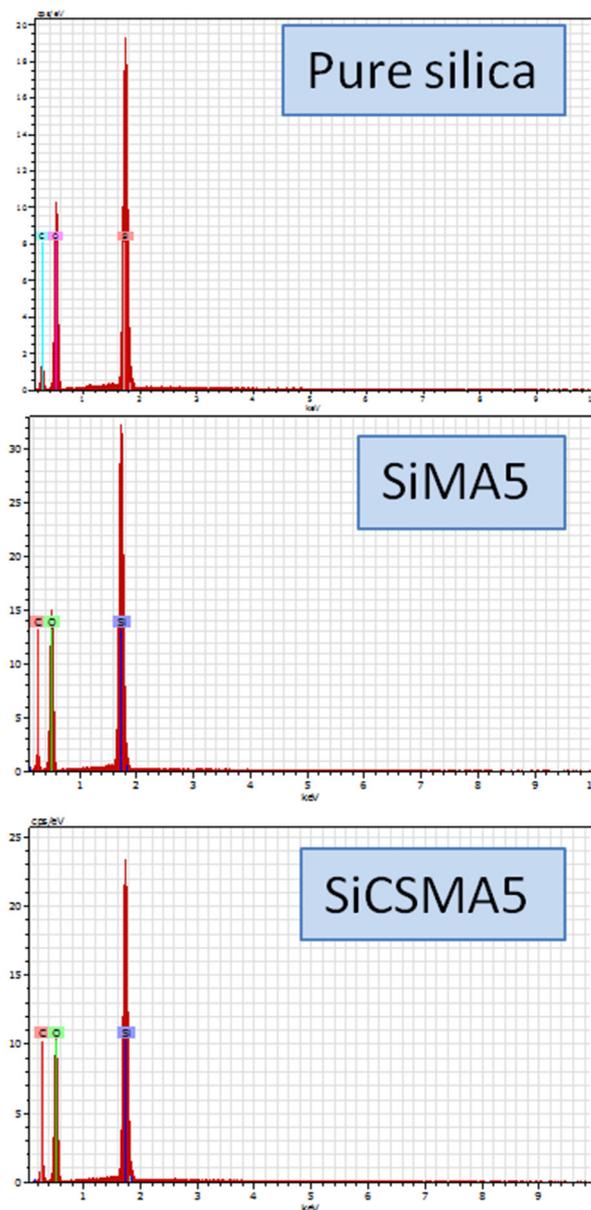


Fig. 6. EDX analysis of some of the obtained hybrid materials – pure silica, SiMA5 and SiCSMA5.

Increased weight change in % showed sample SiCSMA5 in comparison to SiMA5 and SiCS5. The combination of chitosan's property to expand its units and the porosity of MA lead to increasing the weight with 31% after immersion for 48 h and with 45% for 168 h in the water solution. The high sorption capacity of these hybrid materials ensures their improved contact with external ions. The addition of CS to the SiMMA5 hybrid structure didn't change the sorption capacity of the materials. This property showed that SiCSMA5 has long term stability in water media. The results for hybrid SiCSHEMA5 are different comparing them with

the results for the other hybrid samples – the weight change in percent showed, that after immersion for 48 h/168 h of SiCSHEMA5 30%/15% is lost in the solution. These values demonstrated the low stability of this composition, which restrict its application as a sorbent [19–21].

4. CONCLUSIONS

Amorphous silica hybrid materials, with participation of natural and synthetic organic components were successfully obtained via sol-gel route. The investigation of the structural characteristics showed strong dependence on the specific properties of organic units which influence the hybrid structure. The long term stability of the hybrid materials was investigated via immersion in neutral media for 48 h and 168 h. The weight change in percent showed the excellent stability of pure silica, combination of silica and MA, as well as silica and MMA. Lower stability presented the silica hybrid materials with participation of CS and HEMA. In order to find further potential applications of the synthesized hybrid materials, their behaviour in acidic and basic solutions should be investigated, as well as more structural analysis are necessary to be made.

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