Structure of hybrid materials containing natural and synthetic organic compounds

G. E. Chernev\textsuperscript{1}\textsuperscript{*}, E. V. Todorova\textsuperscript{1}, S. P. Djambazov\textsuperscript{1}, I. M. Miranda Salvado\textsuperscript{2}

\textsuperscript{1} Department of Silicate Technology, University of Chemical Technology and Metallurgy, 8 Kl. Ohrydski Blvd. 1756 Sofia, Bulgaria
\textsuperscript{2} Department of Materials and Ceramics Engineering, CICECO, University of Aveiro, Aveiro, Portugal

Received February, 2013; Revised May, 2013

Hybrid materials are innovative and extensively studied, because of the incorporation organic compounds in inorganic network, combining their properties. The properties of the hybrid material can be controlled by variation of the nature and amounts of the components. Recently, the sol-gel synthesis of hybrid materials has been extensively studied due to the possibility of controlling the chemical conditions, as well as it allows the introduction of organic and bioorganic molecules within the inorganic network.

In the present work, results on sol-gel synthesis and structure of hybrid materials containing silica and natural (chitosan) and synthetic (methyl methacrylate) organic compounds are described and discussed. Two and three component hybrid materials were prepared by mixing inorganic precursor – tetraethylortosilicate with the organic components. The structure of the obtained hybrid materials was studied by XRD, FT-IR, SEM and AFM. With the help of SEM the presence of spheres in the synthesized material was observed. The presence of a heterogeneous structure with well-defined nano units was suggested by AFM studies.

Key words: hybrids, sol-gel, silica, chitosan, methyl methacrylate.

INTRODUCTION

Hybrid materials are extensively studied, because of the incorporation organic compounds in inorganic network, combining their properties. Sol-gel method allows to synthesized materials with high homogeneity and purity at a molecule level [1]. Sol-gel process involves hydrolysis of silica precursor and condensation of Si–oH groups into SiO\textsubscript{4} tetrahedra. These building units are bridges by oxygen and lead to formation of Si–O–Si network. Silica materials obtained via sol-gel route exhibit good thermal and mechanical properties and long-term stability at different pH [2, 3]. Thermodynamic stability of Si–O bond enables interactions with many biomolecules and allows them to function normally in the presence of silicates [4]. Many researcher groups work on synthesis of biomaterials (biosensors and biocatalysts) and their interaction effect with different biomolecules–enzymes, proteins, living cells and others [5–7]. Most of them combine inorganic matrix on the base of silica precursors with organic polymers, with potential application in different fields: biotechnology, medicine, optics, pharmacy and etc.

The addition of organic constituent improves the plasticity of the silicate matrix. Furthermore, using sol-gel synthesis we can easily insert functional groups from polymer into the silicate matrix and that will afford entrapment of biomolecules [8].

In the last few years intensive investigations of silicate materials with participation of acrylates [9–11], alginates [12] and polysaccharides have been carried out. Chitosan (CS) is the second most abundant natural polysaccharide, composed of glucosamine and N-acetyl-glucosamine units [13, 14]. It has three reactive groups – primary amino or amide group and secondary hydroxyl groups [15]. Chitosan is insoluble in water and organic solvents, but soluble in acid water solution (pH <6.5) [16]. In low pH conditions amino groups are protonated and become positively charged, which makes CS a cationic polyelectrolyte [17]. Most of the bacteria’s and enzymes are negative charged and can easy form bounds with amino groups of CS [18].
Many investigations for the structure and properties of silica/chitosan hybrid materials are available [19–23]. Si/CS hybrid materials can be used as biomaterials in medicine, pharmacy, as materials for enzyme immobilization, for adsorption of toxic metals and dyes in waste water [24–28] etc.

Materials based on silica and different acrylates lead to formation of hybrids with good protective properties [29]. Adsorption of different biomolecules is limited by the length of the synthetic organic chain. With increasing chain length of acrylates, adsorption of biomolecules decreases.

For improving characteristics of silica/organic hybrids, they can be modified, by using combinations of polymers. Modified by grafting method polysaccharide (chitosan) with synthetic organic compound improves adsorption and mechanical properties of materials [30, 31].

The main objectives of the present study were the synthesis and structural characterization of hybrid materials on the base of silicate matrix, cross linked with chitosan and methyl methacrylate by the sol-gel method.

EXPERIMENTAL

Hybrid materials in the systems silica/chitosan (SiCS), silica/methyl methacrylate (SiM) and silica/chitosan/methyl methacrylate (SiCSM) were prepared using sol-gel method.

Tetraethyl orthosilicate (TEOS) was used as silica precursor, chitosan and methyl methacrylate (MMA) were used as organic constituents. Silica precursor was hydrolyzed in the presence of distilled water (dH2O) and 1 N HCl for 1 hour under vigorous stirring. Ratio of TEOS/dH2O/HCl is kept constant for all mixtures (sol). Chitosan was dissolved in 1% acetic acid and stirred until fully dissolved. Then silica sol was mixed with chitosan solution and MMA, respectively. The ratios between silica/CS and silica/MMA were varied from 1 to 4 wt.%. Obtained hybrid sols (SiCS, SiM, SiCSM) were dried at room temperature until formation of solid gels.

The structure of synthesized hybrid materials was investigated using follow methods:

X-Ray diffraction (XRD) measurements were performed by a bruker D8 Advance. The diffracted intensity of CuKα radiation was measured with scan rate of 0.02°·min⁻¹ in 2θ range between 10 and 80°. Infrared Spectra (FT-IR) were obtained using a MATSON 7000 Forier Transforming Infra Red spectrometer. Pellets of 2 mg of hybrid samples were mixed with 200 mg of spectroscopic grade KBr. Information about surface characteristics of synthesized hybrids was obtained using EDS (Rentec EDS system), SEM (Philips 515) and AFM (Nano Scope Tapping Mode TM).

RESULTS AND DISCUSSION

All synthesized samples were investigated with powder XRD and obtained results are presented on Figure 1. In the three investigated systems a halo is observed at ~ 23° 2θ. This halo shows the amorphous character of the obtained hybrid materials. In the systems with chitosan peak at ~23° 2θ is overlap with anhydrous crystalline form of chitosan.

FT-IR spectra of SiM, SiCS, and SiCSM hybrids are shown on Fig. 2–4. In FT-IR spectra of obtained hybrids characteristic absorption bands of silica network and organic components, as well as new absorption peaks, proved chemical interac-
Fig. 3. FT-IR spectra of SiCS hybrids

Fig. 4. FT-IR spectra of SiCSM hybrids

Fig. 5. SEM and AFM images on the surface of hybrids in the system SiCS
tion between them is detected. As a result of hydrolysis and condensation of TEOS, characteristic peaks at 795, 550 and 458 cm$^{-1}$ corresponding for Si–O–Si symmetric stretching vibration. Intensive peak 1081 cm$^{-1}$ show Si–O–Si asymmetric stretching mode [32]. On the other hand these peaks corresponding to Si–O–C band, which can be prove for new band between silica and organic sources. The presence of free Si–OH mode is associated with peak at 950 cm$^{-1}$. Wide band of absorption in the field of 3400 cm$^{-1}$ related to symmetrical valent vibration of free NH$_2$ and OH groups and H-bonding interactions. Absorption peaks of chitosan at 2980–2850 cm$^{-1}$ (–OH и –СН stretching band) are detected [26]. The decrease in peak intensity around 1250 cm$^{-1}$ is due to co-condensation of –O–H groups of chitosan with silicate matrix [26]. A new absorption peak in spectra of SiCS hybrid at 1643 cm$^{-1}$ can be attributed to the asymmetric N–H deformation vibration and confirm the –NH$_3^+$ ion formation [33].

In the FT-IR spectra of hybrid containing MMA the peak of C=C bond at 1642 cm$^{-1}$ validates the incorporation of MMA in silica network, because no such C = C is present in TEOS.

In the system SiCSM typical characteristic bands of Si–O–Si network are detected, which are widely described above. The peak at 1643 cm$^{-1}$ can be attributed to formation of –NHCO linkage between chitosan and MMA [34]. These results proved cross linking of chitosan in Si-O-Si network and incorporation of two organic components by the grafting method.

The surface of obtained hybrids was investigated by SEM and AFM analysis (Fig. 5–7). All samples had smooth surface with distributed spherical par-

Fig. 6. SEM and AFM images on the surface of hybrids in the system SiM
Formed units proved the incorporation and cross linkage of chitosan in silica network. SEM micrographs of SiCS system (Fig. 5) showed decreasing trend of particle size with increasing amount of chitosan solution.

Influence of partial substitution of chitosan with MMA on the structure is shown on Fig. 7. Adding MMA to Si/CS mixture, rough surface is observed. The change of morphology is due to grafting process between chitosan and MMA. Distribution and spherical size followed the same tendency. Particles with diameter 61 nm at equal amount of inorganic and organic components are formed.

AFM investigations of obtained samples in 2d, 3d topography and roughness analysis are presented on Figures 5, 6 and 7. Samples, containing TEOS and chitosan formed smooth structure, where z-direction increase from 30, 2 nm (SiCS1) to 888, 6 nm (SiCS4). Variations of unit size on their surface are confirmed with roughness analysis (Fig. 5).

AFM topographies of SiCSM hybrid materials presented transformation from smooth (Fig. 7b) to rough surfaces (Fig. 7d) with increasing organic amount. When organic and inorganic components are in equal amount, rough surface with maximum z-direction (10, 4 μm) is observed. From AFM surface analysis can be concluded for random distribution of hybrid units.

CONCLUSIONS

Hybrid materials, containing silica, chitosan and methyl methacrylate were successfully synthesized.
using sol-gel method. Obtained results of XRD proved the amorphous structure of hybrids. FT-IR spectra showed result of hydrolysis and condensation of silica source, formed reactive amino and hydroxyl groups and interaction between methyl methacrylate and chitosan in SiCSM hybrids. SEM images showed random distribution of chitosan in silica network. With increasing amount of organic component formed spherical particles become smaller. Partial replacement of chitosan with methyl methacrylate, formed spherical particles is better distributed in the structure. The existing reactive groups in obtained materials ensured different application of obtained hybrids in the field of biotechnology.

Acknowledgements: The authors are grateful to the CICECO of the Project Pest-C/CTM/LA001/2011 from the University of Aveiro, Portugal for the support.

REFERENCES

G. E. Chernev et al.: Structure of hybrid materials containing natural and synthetic organic compounds

СТРУКТУРА НА ХИБРИДНИ МАТЕРИАЛИ, СЪДЪРЖАЩИ ЕСТЕСТВЕНИ И СИНТЕТИЧНИ ОРГАНИЧНИ СЪЕДИНЕНИЯ

Г. Е. Чернев1*, Е. В. Тодорова1, С. П. Джамбазов1,
И. М. Миранда Салвадо2

1 Катедра „Технология на силикатите“, Химикотехнологичен и Металургичен Университет,
бул. „Климент Охридски“ 8, 1756 София, България
2 Департамент по инженерна керамика, СИСЕКО, Университет на Авеиро,
Авеиро, Португалия

Постъпила февруари, 2013 г.; приета май, 2013 г.

(Резюме)

Хибридните материали са иновативни и широко изучавани материали, поради възможността за съчетаване на неорганична матрица и органични компоненти, което позволява промяна на свойствата на получените материали. Свойствата на хибридните материали зависят от природата и количествата на изходните компоненти. През последните години интересът към синтезиране по зол-гел на хибридни материали е голям, заради възможността условията на синтез да бъдат контролирани, както и внасянето на органични и биоорганични молекули в неорганичната матрица.

В настоящата работа са представени и дискутирани резултатите върху структурните изследвания на хибридни материали синтезирани по зол-гелен метод, съдържащи естествени (хитозан) и синтетични (метил метакрилат) органични компоненти. Синтезирани са дву- и трикомпонентни системи използвайки неорганичен прекурсор-тетраметилоргосиликат и горепосочените органични компоненти. Структурата на получените хибриди е охарактеризирана с помощта на РФА, ИЧ, СЕМ и АСМ анализи.