

COMPOSITION AND THERMAL STABILITY OF SiO₂-BASED HYBRID MATERIALS TEOS–MTEOS system*

*M. Zaharescu**¹, A. Jitianu¹, A. Brăileanu¹, J. Madarász², Cs. Novák²
and G. Pokol²*

¹Romanian Academy, Institute of Physical Chemistry, Bucharest, Romania

²Budapest University of Technology and Economics, Institute of General and Analytical Chemistry, Hungary

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Abstract

Hybrid materials with different amounts of organics permanently bound on the inorganic network obtained in the TEOS–MTEOS (tetraethoxysilan-methyltriethoxysilan) system are used for obtaining coatings with different optical and mechanical properties.

To study the thermal stability of the mentioned materials, compositions with different molar ratios of the precursors were prepared. The influence of the solvent and water amounts on the gelation process was also investigated.

The xerogels obtained were characterised by IR spectrometry and their decomposition was followed by DTA/TG–MS.

Thermal stability of the gels is rather influenced by their composition than the conditions of the gelation process.

Keywords: SiO₂-based hybrid materials, TEOS–MTEOS system, thermal analysis

Introduction

In the whole history of materials until few decades ago only pure organic or inorganic materials were obtained and studied. The development of the sol-gel method allowed for the first time to incorporate organic molecules into the inorganic network without destroying them, leading to the preparation of the hybrid organic-inorganic materials [1, 2].

Silicon-containing hybrid gels can be conveniently synthesised from the precursors such as R_{4-x}Si(OR)_x (x≥1). These precursors led to the so-called ORMOSILs (ORganically MODified SILicates) or ORMOCERs (ORganically MODified CERamics) that were first reported by Schmidt in early 1980s [3].

* It is dedicated to Prof. S. Gál on the occasion of his 70th birthday.

** Author for correspondence: mzaharescu@chemfiz.icf.ro

Sanchez [1] divided conventionally the hybrid materials in two classes:

- Class I corresponds to the hybrid materials in which organic molecules, oligomers or low molecular mass organic polymers, are simply embedded in inorganic matrices;
- Class II of hybrid materials corresponds to the type of the networks where both organic and inorganic compounds are bonded through covalent or iono-covalent chemical bonds.

The first application of the silicon-based hybrid materials from the Class II was realised by Dislich in 1963 [4], who obtained mono-methyl-polysiloxane films with refractive index lower than that of SiO₂. The material was called ‘mono-methylated silica glass’.

Later studies have shown that organic modified alkoxides, such as methyltriethoxysilane (MTEOS), added in the sol-gel systems increase the elasticity of the coatings on different substrates [5, 6]. In the case of the sol-gel glasses it was observed that the density, elasticity modulus, hardness and the fracture toughness increased with the amount of bonded carbon [7, 8].

The first study on the thermal behaviour of MTEOS-based gels was realised by Kamiya *et al.* [9] who performed the study of the decomposition of MTEOS-based gels in air, ammonia and inert atmosphere and proposed a model of decomposition. It was established that the decomposition in air started at 350°C, while in inert atmosphere the gels were stable up to around 700°C.

Matsuda *et al.* [10] studied the variation of different properties of coatings based on the MTEOS-TEOS system (refractive index, hardness, contact angle and the intensity of IR absorption peaks) with the temperature of thermal treatment. They determined that the methyl groups from the films were burned out between 500–600°C.

In our previous papers [11, 12] the thermal stability of hybrid materials obtained from methyltriethoxysilane (MTEOS) and vinyltriethoxysilane (VTEOS) was studied, as well as the aging influence on their thermal stability.

Suyal *et al.* [13] demonstrated that the addition of colloidal silica sol delays the decomposition of methyl groups in MTEOS containing condensate species of gels obtained in MTEOS-TEOS system.

Taking into consideration the differences in the thermal stability of the gels in the TEOS-MTEOS system reported in the literature data, in the present work a systematic study of the correlation between composition and thermal stability of SiO₂-based hybrid materials obtained in the TEOS-MTEOS system was carried out.

Experimental

Sample preparation

As Si-precursors the following alkoxides were used: tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS), all Merck.

The composition of the starting solutions and the conditions of preparation are presented in Table 1. The samples were stored in untight glass vials and left for gelling at room temperature.

Table 1 Composition of starting solutions and experimental conditions of the studied samples

Series	Sample	Moles TEOS	Moles MTEOS	$\frac{\text{EtOH}}{\Sigma\text{alkoxides}}$	$\frac{\text{H}_2\text{O}}{\Sigma\text{alkoxides}}$	Conditions of reaction		Gelling time/h
						pH	T/°C	
1	1a	1.00	0.00	2	1	3.5	25	215
	1b	0.75	0.25	2	1	3.5	25	240
	1c	0.50	0.50	2	1	3.5	25	284
	1d	0.25	0.75	2	1	3.5	25	362
	1e	0.00	1.00	2	1	3.5	25	356
2	2a	1.00	0.00	2	4	3.5	25	–
	2b	0.75	0.25	2	4	3.5	25	–
	2c	0.50	0.50	2	4	3.5	25	–
	2d	0.25	0.75	2	4	3.5	25	–
	2e	0.00	1.00	2	4	3.5	25	–
3	3a	1.00	0.00	4	4	3.5	25	168
	3b	0.75	0.25	4	4	3.5	25	236
	3c	0.50	0.50	4	4	3.5	25	405
	3d	0.25	0.75	4	4	3.5	25	478
	3e	0.00	1.00	4	4	3.5	25	526

Sample characterization

The structure of the obtained gels was determined by XRD and FTIR spectrometry.

The XRD patterns were recorded on a FPM HZ-4 diffractometer using CuK_α radiation with Ni filter.

FT-IR spectra were recorded on Bio-Rad Excalibur FTS 3000 equipment, in the 4000–400 cm^{-1} range. Measurements were made in solid phase using KBr pellets.

The thermal behaviour of the gels was followed up to 700°C using an STD 2960 Simultaneous TG-DTA (TA Instruments); heating rate: 10°C min^{-1} ; flowing air atmosphere: 10 L min^{-1} .

The coupled TG/DTA–MS measurements were carried out in flowing helium atmosphere (130 ml min^{-1} 99.996% He, ThermoStar QS300 Quadrupole mass spectrometer (Balzers) with a deactivated fused silica capillary was connected to the above thermal balance. Ion intensities $m/e=1-64$ were permanently monitored.

Results and discussion

The compositions studied contained understoichiometric (Series 1) and stoichiometric (Series 2 and 3) amounts of water and a low concentration of solvent.

From the three series of solutions prepared in the conditions presented in Table 1 only two of them (Series 1 and 3) had a good homogeneity until gelation. Series 2 of samples presented immiscibility from the moment of the mixing of the components.

In order to ensure a satisfactory homogeneity of the samples with stoichiometric amount of water it was necessary to increase also the amount of solvent for Series 3.

Structural characterization of the obtained gels

The gels were amorphous as observed by XRD.

The FT-IR spectra of the gels from Series 1 are presented in Fig. 1 (a–e) and of the gels from Series 3 in Fig. 2 (a–e).

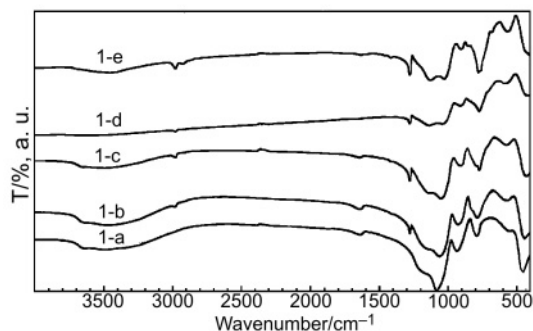


Fig. 1 FT-IR spectra of the gels from Series 1

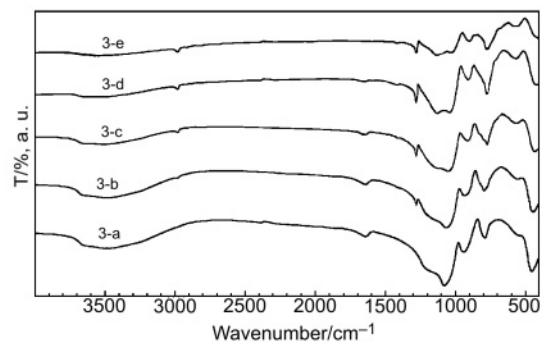


Fig. 2 FT-IR spectra of the gels from Series 3

In both series, the gels obtained starting only with TEOS present the characteristic vibration bands of a SiO_2 gel, mainly: $\nu_{\text{as}}\text{Si-O-Si}$ (LO) at 1200 cm^{-1} ; $\nu_{\text{as}}\text{Si-O-Si}$ (TO) at 1089 cm^{-1} ; $\nu_{\text{as}}\text{Si-O(H)}$ at 946 cm^{-1} ; $\nu_{\text{s}}\text{Si-O-Si}$ at 795 cm^{-1} ; $\nu\text{Si-O-Si}$ at 540 cm^{-1} and $\delta\text{Si-O-Si}$ at 461 cm^{-1} [14]. None of ν_{CH} vibration bands occurred in samples 1a and 3a.

In case of the gels obtained with MTEOS and of those obtained in the TEOS–MTEOS system besides vibration peaks characteristic for the silica network the characteristic vibration bands of the organic groups present in the gels could be noticed. Capozzi *et al.* [15, 16] showed that in case of the gels prepared with MTEOS the peak from 780 cm^{-1} represent a superpose of two characteristic peaks for $\nu_{\text{s}}\text{Si-O-Si}$ and also for $\nu_{\text{s}}\text{Si-C}$ vibrations. In the same time the $\nu_{\text{s}}\text{Si-O-Si}$ LO (1129 cm^{-1}) and $\nu_{\text{s}}\text{Si-O-Si}$ (780 cm^{-1}) bands are shifted towards lower wavenumbers

as compared to the similar bands in pure TEOS based gels and this shift increases progressively with the increase of the MTEOS amount in the initial reaction mixtures. This fact could prove that Si–C bonds exist in the final gels and that the above mentioned overlap is real [15–17]. Also, one can point out that the band characteristic for $\nu\text{Si–O(H)}$ present at 946 cm^{-1} in pure TEOS-based gels is shifted to lower wavenumbers and decrease in intensity with the increase of MTEOS amount for both series of the studied gels. This observation can be explained by the fact that with the increase of MTEOS amount the hydrophobicity of these materials increases.

The specific bands for the presence of CH_3 groups bonded at silicon atoms were: $\nu_{\text{as}}\text{CH}_3$ at 2976 cm^{-1} ; $\nu_{\text{s}}\text{CH}_3$ at 2912 cm^{-1} , $\delta_{\text{as}}\text{C–H}$ at 1414 cm^{-1} ; $\delta_{\text{s}}\text{C–H}$ at 780 cm^{-1} . For the gels obtained in TEOS–MTEOS system it could be observed that the intensity of the specific bands assigned to the presence of CH_3 and CH_2 groups bonded at silicon atoms (2976 and 2912 cm^{-1}) increases with increasing of the quantity of MTEOS.

The silica network of the pure TEOS gels, in both series, is very well developed. With increasing of MTEOS amount an increased degree of disordering of the silica network was observed.

Thermal behaviour of the gels obtained

Thermal behaviour in air

The DTA/TG results for all the samples studied are summarized in Table 2.

The gel obtained starting only with TEOS in both studied series behaves practically as a common silica xerogel. It starts the water evolution at about 80°C and no organics evolution is noticed during the heating at all.

The gel obtained only with MTEOS, in both studied series, is more or less stable up to about 350°C , then it decomposes with a significant amount of organics evolution over 400°C . The decomposition is accompanied by an exothermal effect, due to the burning out of the organic radicals bounded on the inorganic network. The behaviour is that of an organic modified silica gel and is in good agreement with the data previously reported [11, 12].

The gels in the binary TEOS–MTEOS system, obtained in both Series 1 and 3, with under-stoichiometric and stoichiometric amounts of water, respectively, present a slight but systematic increase of the temperature of decomposition with the increasing of the amount of TEOS in the mixtures. This fact could be explained by the fact that with the increase of the inorganic part/organic part ratio of the whole network the decomposition of the organics is shifted to higher temperatures.

The obtained results are in good agreement with the results reported by Suyal *et al.* [13] which shows that the addition of colloidal SiO_2 as a component of the sol stabilizes the CH_3 group against the decomposition.

With the increase of MTEOS amount, in both series, the mass loss in the first step of the decomposition decreases, indicating that this step is related mainly to the decrease of water content of inorganic part of the gels. In the same time, the mass loss in the further steps increases, being related to the decomposition and the burning out of the organic component of the gel.

Table 2 Thermal behaviour of the studied gels

Series	Sample	Temperature range/°C	Thermal effect/°C		Mass loss/%	Assignment
			Endo	Exo		
1	1a	20–172	94	–	9	Water evolution
		172–700			7.5	Structural water evolution
	1b	20–166	69	482	7.46	Solvent and water evolution
		166–354			3.90	Decomposition
	1c	354–700	67	473	5.58	Burning out of the organic residues
		20–152			4.76	Solvent and water evolution
	1d	152–340	64	467	4.21	Decomposition
		340–700			7.57	Burning out of the organic residues
	1e	20–147	78	–	3.65	Solvent and water evolution
		147–360			4.61	Decomposition
3a	360–700	72	484	8.08	Burning out of the organic residues	
	20–110			0.7	Solvent and water evolution	
3b	110–328	68	477	4.7	Decomposition	
	328–700			13.64	Burning out of the organic residues	
3c	20–168	65	467	13.13	Water evolution	
	168–700			3.76	Structural water evolution	
3d	20–161	65	467	9.46	Solvent and water evolution	
	161–350			2.47	Decomposition	
3e	350–700	65	467	3.50	Burning out of the organic residues	
	20–158			7.04	Solvent and water evolution	
3	158–363	65	467	3.32	Decomposition	
	363–700			5.45	Burning out of the organic residues	
3	20–138	65	467	3.27	Solvent and water evolution	
	138–331			3.54	Decomposition	
3	331–700	65	467	8.65	Burning out of the organic residues	
	20–110			1.44	Solvent and water evolution	
3	110–304	65	467	5.10	Decomposition	
	304–700			12.78	Burning out of the organic residues	

Thermal behaviour in pure helium atmosphere

Thermal analysis curves of the samples 1c and 1e, performed in He atmosphere, are presented in Figs 3 and 4, respectively.

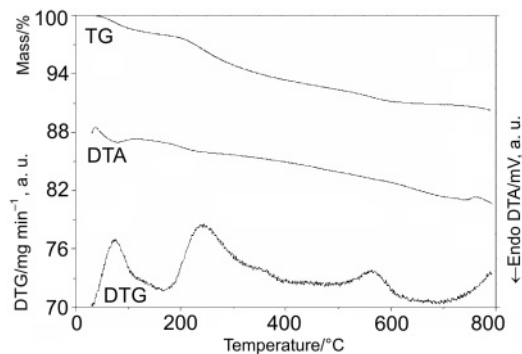


Fig. 3 Thermal behaviour of sample 1c in inert atmosphere (He)

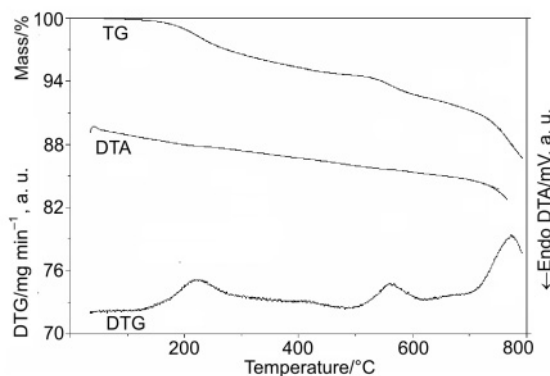


Fig. 4 Thermal behaviour of sample 1e in inert atmosphere (He)

Both gels have quite similar thermal behaviour, except the effect around 80°C present only for the sample 1c, assigned to solvent and adsorbed water evolution. Sample 1e does not show this effect because of the hydrophobicity and low porosity of the MTEOS-based gel.

The mass loss with the maximum at around 200°C is probably due to the chemically bounded water (i.e., the decomposition of structural OH groups) and is more evident in the case of sample 1c which contains TEOS, where the amount of -OH is supposed to be higher. According to the coupled MS monitoring, the evolution peaks of H₂O fragment ions ($m/e=17-18$) occurred at the above mentioned temperatures. Various ion fragments of CH₃CH₂OH and ethylene oxide are also observed at low levels between 50 and 320°C in both cases.

The effect at around 560°C may be assigned to the breaking out of residual -OC₂H₅ groups as ethylene and methane shown by their ion fragments. The effect is more evident

for sample 1e, prepared only with MTEOS, which due to its hydrophobicity may contain more unhydrolyzed $-\text{OC}_2\text{H}_5$ groups.

The temperature of $\text{Si}-\text{CH}_3$ decomposition in sample 1e is displaced over 700°C , in good agreement with Kamiya's results [9] and with our MS-findings. In sample 1c, that contains TEOS, due to the increase of the inorganic part/organic part ratio of the whole network, the temperature of decomposition is displaced over 800°C .

Conclusions

In the present work a systematic study of the correlation between composition and thermal stability of SiO_2 -based hybrid materials obtained in the TEOS–MTEOS system was carried out.

In air, a slight but systematic increase of the $\text{Si}-\text{CH}_3$ temperature of decomposition with the increasing of the amount of TEOS in the mixtures was observed, explained by the increase of the inorganic part/organic part ratio of the whole network in the gels.

In inert atmosphere (He), the temperature of $\text{Si}-\text{CH}_3$ decomposition is displaced to significantly higher temperatures proved by evolution of CH_4 observed by a coupled MS system.

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