Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 1, 19–26

THE INTERACTION BETWEEN TEOS AND SOME POLYOLS
Thermal analysis and FTIR

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Hybrid organic-inorganic materials, silica – polyols (ethylene-glycol – EG; 1,2 propane diol – 1,2PG; 1,3 propane diol – 1,3PG and glycerol – GL), were prepared by a sol-gel process starting from tetraethylorthosilicate (TEOS) and polyols, in acid catalysis. The resulting materials were studied by thermal analysis (in air and nitrogen), FTIR and solid state ^{29}Si-NMR spectroscopy. These techniques evidenced the presence of polyols in the silica matrix both hydrogen bounded and chemically bounded in the silica network. The thermal analysis proves to be the most appropriate technique to evidence the organic chains linked in the matrix network and to follow the thermal evolution of the gels to the SiO_2 matrix.

Keywords: *hybrid, polyol, silica, thermal analysis*

Introduction

It is well known in the special literature that the sol–gel method is a practical and promising way to obtain porous materials by a relatively simple proceeding. The relationships between working conditions and the obtained micro- and mesoporous structures involve a particular interest from practical point of view and they have been intensively studied [1–3]. In order to control the porous structure of the resulting materials, the sol-gel method was used to synthesize hybrid gels: silica-organic compounds, the last ones being afterwards eliminated by combustion, with obtaining of silica matrixes with controlled porous structures [4–7].

From the standpoint of interactions at the interface between organic and inorganic compounds, we distinguish between two classes of hybrids. First class includes hybrids in which the interaction between organic and inorganic constituents is weak and is due to secondary forces (van der Waals, hydrogen bounds and electrostatic forces). Second class concerns hybrids in which the interaction between organic and inorganic constituents is strong and is due to covalent bonds [4, 8].

Hybrid materials may be synthesized, by introducing in the SiO_2 matrix some monomers, oligomers or organic polymers which contain polar groups, such as: formamide [9], ethylene glycol [10–12], polyethylene glycol [13] or poly(vinylalcohol) [14].

In the literature, the effect of organic additives on the gelling process (hydrolysis and condensation) and on the gels final structure is explained through hydrogen bonds formation with water and silanol groups [9, 11, 12, 15, 16].

Previous studies on the tetramethoxysilane (TMOS) – ethylene glycol (EG) (and polyethylene glycol – PEG) system, established the influence of these additives on the pores, for molar ratios of EG (PEG):TMOS<5. The interaction mechanism between these additives with TMOS and its hydrolysis products was not exactly established at that moment [12].

Ravanie *et al.* [17] have studied the system TEOS : PEG : HCl. They observed that ethoxy groups of TEOS interact with hydroxyl groups of PEG, leading to products with different substitution degrees of PEG in TEOS forming Si–O–C covalent bonds. This hypothesis was also accepted by Shilova *et al.* [2] studying the influence of –OH groups containing additives, on the stability of TEOS based sol–gel systems and on the structure of hybrid organic-inorganic coverings.

In this article we provide a thermal analysis study (in air and nitrogen atmosphere) on the interaction of some polyols (ethylene glycol – EG, 1, 2 propane diol – 1,2PG, 1, 3 propane diol – 1,3PG, glycerol – GL) with TEOS and its hydrolysis products in the gelling and formation of silica matrix phase. From previous studies [18] we have observed that thermal analysis is an appropriate technique to emphasize the chemical interactions of polyols with silanol groups during the hybrid matrix formation.

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1388–6150/$20.00

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We also follow the polyol – TEOS interaction effect on the morphology of the inorganic matrix, obtained after the suitable thermal treatment.

Experimental

Synthesis

The materials used for the gels synthesis were of analytical grade purity (Merck): ethylene glycol, absolute ethanol, tetraethylorthosilicate, concentrated HNO_3.

The synthesis of the hybrid matrix was performed by addition of ethanolic TEOS solution, at room temperature, under intense magnetic stirring to the acidulated ($c(HNO_3)=0.01$ mol L^{-1}) polyol hydroalcoholic solution. After stirring, the resulting clear solution was maintained under stirring another 30 min, after which it was left gelling at room temperature.

There were synthesized gels without polyol, based on TEOS with water (X_0^4) and without water (X_0^0), in acid catalysis (HNO_3).

There were also synthesized gels with polyols, at molar ratio polyol/TEOS=1:1 and molar ratio H_2O/TEOS=4:1 for the polyols: EG (sample X_1^4), 1,2PG (sample X_2^4), 1,3PG (sample X_3^4) and GL (sample X_4^4).

For EG we have synthesized gels with different water content: without water (sample X_1^0), ratio H_2O:TEOS=4:1 (sample X_1^4) and for H_2O:TEOS=8:1 (sample X_1^8). The synthesized samples composition and their characteristics are presented in Table 1.

After gelling, the obtained gels were crushed in a mortar and dried at the temperature of 40°C for 10 h. Some of the dried gels were, then, thermally treated at 100, 200 and 250°C.

The resulted samples were analysed by thermal analysis (TG, DTA), FTIR spectrometry and ^{29}Si–NMR on solids. Specific surface areas were measured for samples synthesized with and without polyols, thermally treated at 250°C.

Experimental techniques

Thermal analysis was achieved with a 1500 D MOM Budapest derivatograph, in static air atmosphere or dynamic N_2 atmosphere (flow rate 30.0 mL min^{-1}), heating rate 5°C min^{-1}, for temperature range 20–500°C and 10°C min^{-1}, for temperature range 20–1000°C, using α-Al_2O_3 as inert material and Pt crucibles in form of plates.

The FTIR spectra were registered with a JASCO 430 FTIR spectrometer, in KBr pellets, in the domain 400–4000 cm^{-1}.

The ^{29}Si–NMR spectra were measured on a Bruker MSL300 (7.05 T), at a frequency of 59.53 MHz. The spectra were achieved using TMS as reference. There was used a probe of 7.5 mm at a speed of 4 KHz.

The specific surface measurements were achieved with a MICROMERITICS ASAP 2000. The temperature used to outgas the sample was 250°C.

Results and discussion

Our researching into the synthesis of some glyoxylate complexes embedded in silica matrix, obtained by the reaction between metallic nitrates and ethylene glycol (EG) provided that EG interacts with the hydrolysis products of TEOS during the formation of the silica matrix [19, 20].

To clear up this aspect, we have done some thermal analysis and FTIR studies, on the evolution of the system EG–TEOS–H_2O, in acid catalysis, during the formation of the silica matrix [18].

In this paper we present a study on the interaction between TEOS and its hydrolysis products with different polyols (EG, 1,2PG, 1,3PG, GL) in acid catalysis, as well as the influence of the molar ratio TEOS:H_2O on this interaction and on the silica matrix formation.

Table 1 The amounts of the reactants and some characteristics of the gels

Sample	Polyol	Quantity (mole)					Molar ratio	t_{gel}
		TEOS	Polyol	EtOH	H_2O	HNO_3	TEOS:Polyol:H_2O	(h)
X_0^0	–	0.045	–	0.130	–	$1.5\cdot10^{-4}$	1:0:0	280
X_0^4	–	0.045	–	0.130	0.180	$2.0\cdot10^{-4}$	1:0:4	120
X_1^0	EG	0.045	0.045	0.130	–	$2.5\cdot10^{-4}$	1:1:0	114
X_1^4	EG	0.045	0.045	0.130	0.180	$2.5\cdot10^{-4}$	1:1:4	162
X_1^8	EG	0.045	0.045	0.130	0.360	$2.5\cdot10^{-4}$	1:1:8	200
X_2^4	12PG	0.045	0.045	0.130	0.180	$2.5\cdot10^{-4}$	1:1:4	144
X_3^4	13PG	0.045	0.045	0.130	0.180	$2.5\cdot10^{-4}$	1:1:4	240
X_4^4	GL	0.045	0.045	0.130	0.180	$2.5\cdot10^{-4}$	1:1:4	80

Thermal analysis

In order to evidence the influence of polyols, in the TEOS–H_2O system, during the silica matrix formation, we have first synthesized the silica matrix under different conditions: X_0^0, at molar ratio TEOS:H_2O=1:0 and X_0^4 at molar ratio TEOS:H_2O=1:4, both in acid catalysis.

Figure 1 presents the TG and DTA curves corresponding to the two gels, X_0^4 and X_0^0, thermally treated at 200°C.

On the TG curve for the gel X_0^0 (without water), we observe in the temperature range 250–400°C, a mass loss of 9% accompanied by an exothermic effect at 315°C which may be attributed to the combustion of ethoxy groups from the silica matrix [21].

For the gel X_0^4, we can observe a mass loss of 10% on the TG curve in the temperature range 50–150°C, due to the elimination of adsorbed water and volatile products resulted in the condensation reaction. This process is accompanied by an endothermic effect on the DTA curve. Over 150°C, on the TG curve we can notice a slow mass loss, corresponding to the polycondensation reactions promotion, with elimination of the resulted volatiles products.

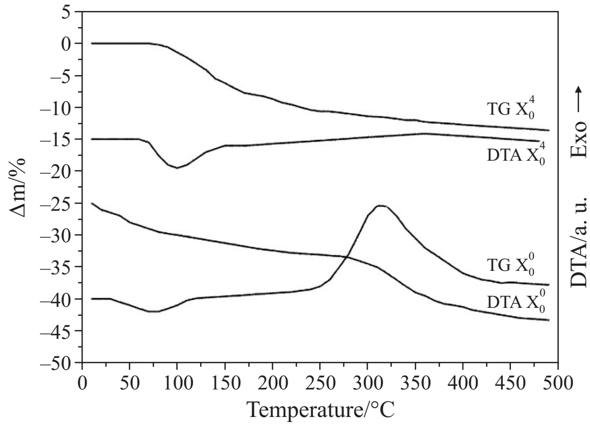

Fig. 1 The thermal curves TG and DTA of the gels X_0^4 and X_0^0, thermally treated at 200°C

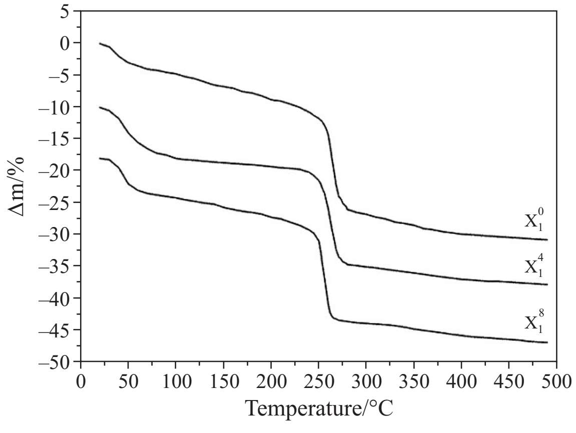

Fig. 2 The TG curves of the gels X_1^0, X_1^4 and X_1^8, thermally treated at 200°C

From thermal analysis, results that the matrix X_0^0 (without water) is a matrix with ethoxy groups, while the matrix X_0^4 contains mainly silanol groups.

For the TEOS–EG–H_2O system, our previous studies for a molar ratio 1:1:4, have shown that in the matrix formation process, EG chemically interacts with the silanol groups, forming a hybrid matrix, in which the organic chain is bounded with the Si atom through Si–O–C covalent bonds [18]:

$$\text{Si–OH+HO–CH}_2\text{–CH}_2\text{–OH} \Leftrightarrow \text{Si–O–CH}_2\text{–CH}_2\text{–OH+H}_2\text{O} \qquad (1)$$

$$\text{Si–O–CH}_2\text{–CH}_2\text{–OH+HO–Si} \Leftrightarrow \text{Si–O–CH}_2\text{–CH}_2\text{–O-Si+H}_2\text{O} \qquad (2)$$

To follow the influence of water on the polyols interaction with TEOS and with its hydrolysis products, we have studied gels TEOS:EG:H_2O with different water content.

Figure 2 shows the TG curves for the synthesized gels with EG at a molar ratio TEOS:EG=1:1, but with different r=H_2O:TEOS molar ratio, thermally treated at 200°C: the gel X_1^0, r=0, the gel X_1^4, r=4 and the gel X_1^8, r=8.

We observe on all the three curves significant mass losses, in a narrow temperature range (250–280°C). This mass losses are attributed to the combustion of the organic chains (–O–CH_2–CH_2–O–) interspersed in the matrix network, being accompanied by wide exothermic effects.

From the presented ones, results that EG interacts with the functional groups of the matrix through Si–O–C links, in both gels synthesized, with water (X_1^4 and X_1^8), containing a high concentration of silanol groups (Si–OH), and without water (X_1^0) with a high concentration of ethoxy groups (Si–OC_2H_5) (Fig. 1).

For the gels X_1^4 and X_1^8, EGs interaction with the hydrolysis products of TEOS is given by the Eqs (1) and (2), but for the gel X_1^0, the interaction of EG with TEOS develops, probably, after a different mechanism.

According to the literature [2, 17, 22], the reaction between the ethoxy groups of TEOS [2, 17] and the hydroxyl groups of diols may lead to species of different substitution degrees of diols in TEOS.

In case of gel X_1^0, without water, the interaction of EG with TEOS may take place according to the following mechanism:

$$\text{Si(OC}_2\text{H}_5\text{)}_4\text{+HO–CH}_2\text{–CH}_2\text{–OH} \Leftrightarrow \text{Si(OC}_2\text{H}_5\text{)}_3\text{(OCH}_2\text{CH}_2\text{OH)+C}_2\text{H}_5\text{OH}$$

$$\mathrm{Si(OC_2H_5)_3(OCH_2CH_2OH)+Si(OC_2H_5)_4 \Leftrightarrow}$$
$$\mathrm{(C_2H_5O)_3Si{-}OCH_2CH_2O{-}Si(OC_2H_5)_3+C_2H_5OH}$$

resembling to the one from the literature [17].

These interactions explain, the shorter gelling period for the gel X_1^0 – 114 h, compared to the gels synthesized with water (X_1^4 – 162 h, respectively X_1^8 – 200 h) and to the gel synthesized without water and without EG: X_0^0 – 280 h.

From the mass losses observed in the range 250–280°C on the three TG curves (Fig. 2), we notice that the ratio TEOS:H_2O used in the synthesis (which determines the nature of the matrix) does not influence, significantly, the EG quantity which chemically bounds in the silica network.

To pursue the interaction of TEOS with different polyols in the formation process of the silica matrix, we have synthesized gels TEOS:H_2O:polyols (EG, 1,2PG, 1,3PG, GL) at a molar ratio 1:4:1, which was established, based on the results presented in the upper part.

During the gelling process (hydrolysis, polycondensation), the polyols which are present in the system TEOS–H_2O may interact with the hydrolysis products of TEOS both through hydrogen bonds and chemically, interspersing in the matrix network. During the thermal treatment of the synthesized xerogels, the polycondensation process advances, at the same time with the elimination of resulted volatile products. At 200°C we may consider that we have a hybrid matrix as a consequence of polyols interspersing in the silica matrix.

The polyols interaction with the hydrolysis products of TEOS may differently take place, depending on the polyols structure (type and number of –OH groups in the molecule).

Figure 3 presents the TG and DTA curves obtained at thermal analysis, in air, until 500°C, of the gels that were thermally treated at 200°C synthesized with EG-sample X_1^4 (Fig. 3a), with 1,2PG-sample X_2^4 (Fig. 3b), with 1,3PG-sample X_3^4 (Fig. 3c) and GL-sample X_4^4 (Fig. 3d).

In all four cases, the process with mass loss, in the 250–350°C range, is attributed to the oxidative decomposition of the organic chains corresponding to the polyols interspersed in the silica matrix. The process is accompanied by a corresponding exothermic effect.

The mass losses observed until 250°C are due to the elimination of the adsorbed water as well as to the elimination of volatile products resulted from the polycondensation reaction.

In the 350–500°C range, the slow mass loss can be attributed to the polycondensation reactions promotion, the final residue presenting a brownish color due to the residual products resulted from the combustion process of the organic part from the matrix. However, at thermal treatment of the gels, in air, until 1000°C, the obtained powders were white, as a consequence of the complete burning of residual products.

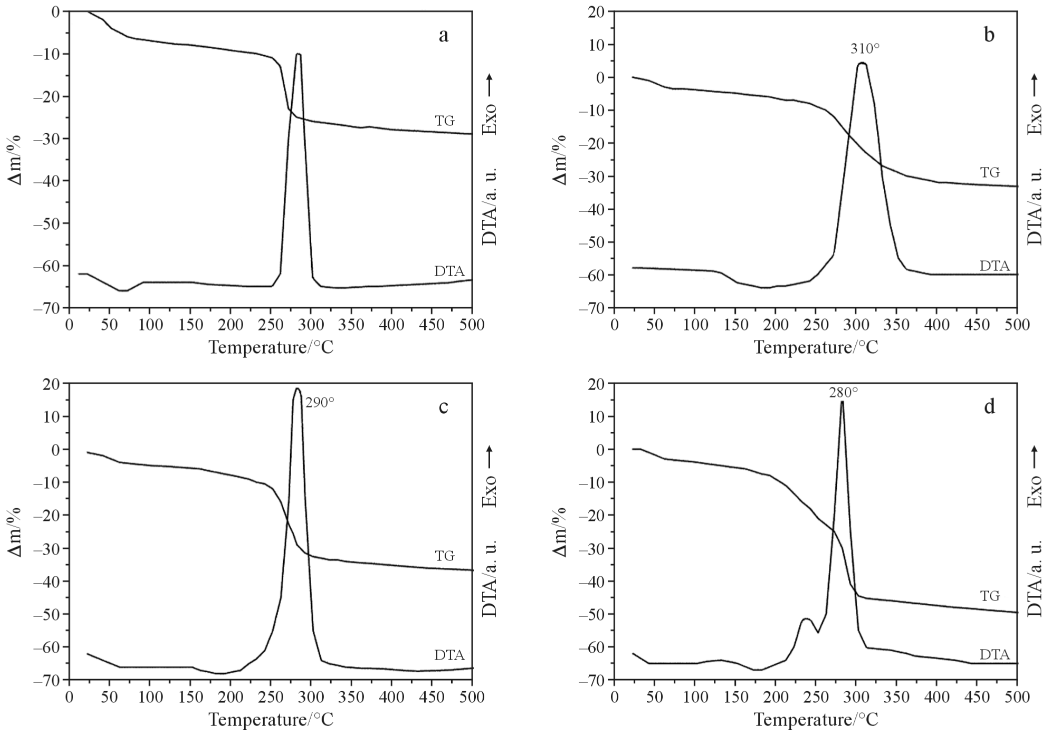

Fig. 3 TG and DTA curves obtained at thermal analysis, in air, of the gels thermally treated at 200°C a – X_1^4 with EG; b – X_2^4 with 1,2PG; c – X_3^4 with 1,3PG; d – X_4^4 with GL

At air heating of the gels X_1^4 and X_3^4, we can notice that the oxidative decomposition of the organic part chemically bounded in the matrix, develops similar, in the same temperature domain, with a strong exothermic effect. This could be explained by the resembling structure of the two diols (EG and 1,3PG), which interact with the matrix through the two primary –OH groups, after a similar mechanism, with Si–O–C bonds formation of near thermal stability.

In case of gel X_2^4 with 1,2PG, in which the diol chemically bounds in the matrix by a primary –OH group and also by a secondary –OH group, the oxidative decomposition process of the organic part is slow, with a larger exothermic effect at 320°C. This can be due to the different thermal stability of the formed Si–O–C bonds.

For the gel X_4^4 with GL, the curves shape is different compared to the curves of the gels with the other polyols. The oxidative decomposition of organic chains resulted from glycerol interspersing in the matrix network, accompanied by an exothermic effect at 290°C. This process is preceded in the range 200–250°C by a mass loss, attributed to the elimination of glycerol remained in the pores, due to its high boiling point (293°C) comparative to the other polyols.

This mass loss is accompanied by an exothermic effect with the maximum at 230°C, which can be explained by the tendency of glycerol (strongly adsorbed at the silanol groups from the pores volume) to decompose at high temperatures [23].

The results obtained for the four studied gels are presented in Table 2.

We can observe that the mass loss from stage (*ii*), corresponding to the oxidative decomposition of the organic groups bounded in the network, depends on the size of the polyols chain.

The presence in the silica matrix of chemically bounded organic chains was also evidenced by thermal analysis until 1000°C, in nitrogen atmosphere, of the gels X_1^4, X_2^4, X_3^4 and X_4^4 thermally treated at 200°C. The TG curves obtained in these conditions are presented in Fig. 4. One can observe from the TG curves, that the mass loss, corresponding to non-oxidative decomposition of chemically bounded organic chains, are achieved in the range 400–600°C, independent on the polyol used in synthesis. The DTA curves registered were similar for all samples.

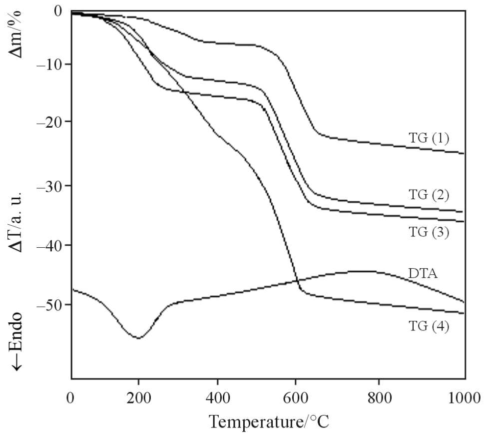

Fig. 4 TG and DTA curves obtained at thermal analysis, in nitrogen, of the gels: 1 – X_1^4, 2 – X_2^4, 3 – X_3^4 and 4 – X_4^4

Until 400°C, the mass loss corresponds to elimination of water, of volatile products from the polycondensation reaction as well as to volatilization of polyols from the pores.

In the temperature range 600–1000°C, the mass of the samples modifies a little due to the polycondensation reactions promotion. The residues are black, as a consequence of residual carbon resulted after the decomposition of the organic part.

FTIR analysis

By FTIR analysis we have followed to evidence the presence of polyols in the silica matrix.

Figure 5 shows the FTIR spectra of the gels: X_0^4 (without polyol) and X_1^4, X_2^4, X_3^4, X_4^4 (with polyol), thermally treated at 200°C. At this temperature, the gels X_1^4, X_2^4, X_3^4 and X_4^4 contain organic chains corresponding to the polyols chemically bounded in the matrix.

The bands which confirm their presence, in the gels treated at 200°C, are those from the ranges 3000–2800 and 1400–1300 cm^{-1}, corresponding to the characteristic vibrations of the bond C–H from the CH_2 and CH_3 groups [24]. The other bands are overlapped with the silica matrix bands.

Table 2 Mass losses, on temperature intervals, until 500°C, in air, of the gels obtained at 200°C

	Sample	*i*		*ii*		*iii*		Residue/%
		T/°C	Δ*m*/%	*T*/°C	Δ*m*/%	*T*/°C	Δ*m*/%	
air 500°C	X_1^4	20–250	8	250–290	16	290–500	3	73
	X_2^4	20–250	9	250–350	22	350–500	3	66
	X_3^4	20–250	9	250–300	24	300–500	3	64
	X_4^4	20–250	23	250–300	25	300–500	2	50

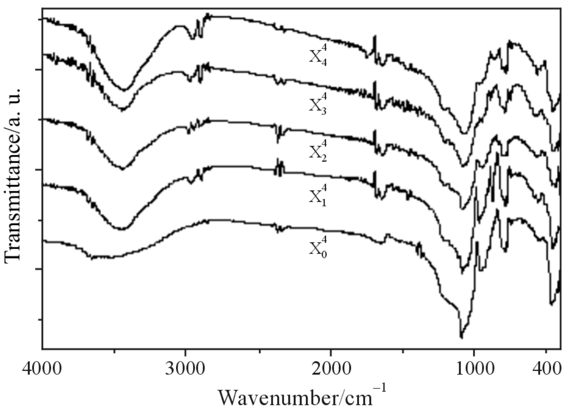

Fig. 5 FTIR spectra of the gels X_0^4 (without polyols), and X_1^4, X_2^4, X_3^4, X_4^4 (with polyols), thermally treated at 200°C

The obtained FTIR spectra were processed through deconvolution, the obtained absorption bands being presented in Table 3.

From the results presented in Table 3, we notice that the gel X_0^4 presents only the bands characteristic to the silica matrix. In case of the other gels (with polyols), the bands characteristic to the vibrations of C–H bond appear, as well as a band of weak intensity in the range 840–890 cm^{-1}, which can be attributed, according to the literature [29], to the vibration of the C–C bond.

Solid state ^{29}Si–NMR

The studied gels were also characterized by solid state Si–MNR spectrometry, in order to describe the local surrounding (proximities) of the Si atom inner the matrix.

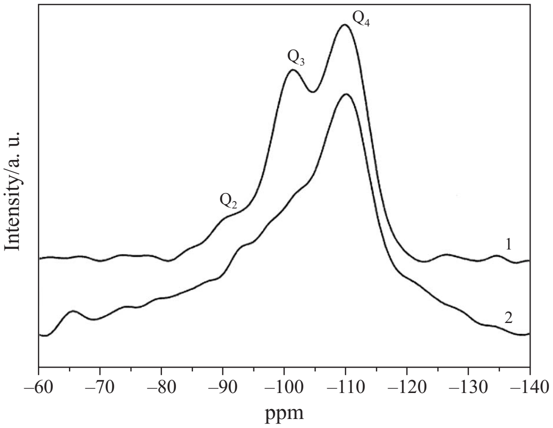

Fig. 6 ^{29}Si–NMR spectra for the gels dried at 100°C: 1 – X_0^4 (without polyol) and 2 – X_1^4 (with EG)

In Fig. 6 are presented the Si–NMR spectra for the gels X_0^4 (without polyol) and X_1^4 (with EG) dried at 100°C.

From the presented spectra, we can observe that in case of X_0^4 the following species are present in the system: Q^4=Si–(OSi)$_4$ (–110 ppm), Q^3= XO–Si–(OSi)$_3$ (–100 ppm) and in lower proportion the species Q^2=(XO)$_2$–Si–(OSi)$_2$ (shoulder from –92 ppm) which indicates the presence of –OH groups at the gels surface [23]. In case of the gel with EG, dried at 100°C, the species Q^4, Q^3, Q^2, Q^1 were identified as a result of the spectra deconvolution obtained by Gaussian signals. This indicates a lower condensation degree, as a result of the H bonds between EG and the silanol groups.

In Fig. 7 are presented the Si–NMR spectra of the gels with different polyols, thermally treated at 200°C, when the polyol is chemically bounded in the

Table 3 The main bands registered in the spectra of the gels X_1^4, X_2^4, X_3^4 and X_4^4 obtained at 200°C

Wavenumber/cm^{-1}					Assignment
X_0^4	X_1^4	X_2^4	X_3^4	X_4^4	
3472	3442	3446	3440	3443	H_2O [25]
	2960, 2893	2980, 2942, 2889	2968, 2897	2950, 2890	C–H [23]
				1727	C=O [9]
1640	1640	1643	1644	1639	H_2O [25,26]
	1460	1455, 1418, 1390	1452, 1420, 1390		C–H (CH_2, CH_3) [25, 26]
	1202	1205	1207	1207	Si–O–Si [25]
			1166		Si–O–C [23, 27]
1085	1081	1087	1086	1078	Si–O–Si [25, 26]
950	960	946	950	960	Si–O(H) [28]
	880	840	889	860	C–C [29]
796	790	794	796	796	Si–O–Si [25, 26]
540	565	570	570	568	Si–O–Si [25]
470	460	460	450	450	Si–O–Si [25, 26]

Table 4 The results obtained at ^{29}Si–NMR analysis of the synthesized gels

Sample	Q^4		Q^3		Q^2		Q^1	
	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%
X_0^4 (100°C)	–109.9	54.7	–100.9	33.3	–92.1	12.0	–	–
X_1^4 (100°C)	–118.4 –110.1	45.0	–102.6	31.3	–92.7	12.2	–82.47	11.5
X_1^4 (200°C)	–109.6	54.8	–101.2	35.8	–92.4	9.4	–	–
X_2^4 (200°C)	–111.3	65.4	–102.3	30.4	–94.6	4.2	–	–
X_3^4 (200°C)	–118.1 –109.2 –114.1	60.9	–103.1 –99.2	29.7	–93.3	9.4	–	–

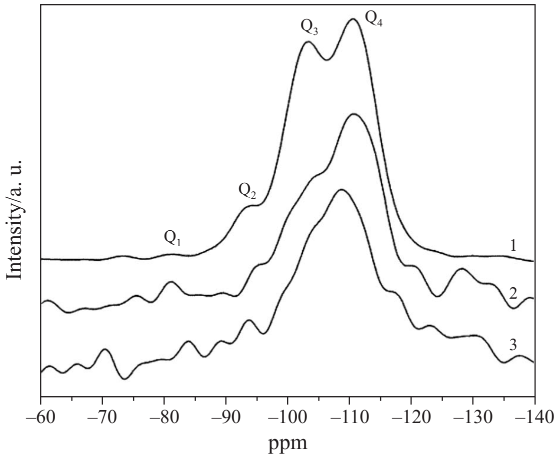

Fig. 7 ^{29}Si–NMR spectra of the gels with different polyols, thermally treated at 200°C: 1 – X_1^4, 2 – X_2^4 and 3 – X_3^4

matrix: X_1^4 – with EG, X_2^4 – with 1,2PG and X_3^4 – with 1,3PG. The species Q^4, Q^3 and Q^2 are present in all the three spectra. The spectra were submitted to deconvolution with signals of Gaussian type, and the results obtained after the processing are presented in Table 4.

From the results presented in Table 4, we can observe that the condensation degree for the gel G1 (with EG), increases with increasing temperature from 100 to 200°C, due to the higher polycondensation and to the elimination of free and hydrogen bounded EG. At this temperature, in the matrix remains only EG chemically bounded. In case of gels with different polyols, thermally treated at 200°C, the condensation degree depends on the polyols nature. For 1,2PG the condensation degree is lower.

The results of ^{29}Si–NMR analysis confirm the conclusions obtained by thermal analysis about the formation of the silica matrix in the presence of the studied polyols.

Specific surface area measurements

In order to follow the effect of chemical interaction between polyols and silica matrix, the specific surface areas of the following gels were determined: X_0^4 (without polyol) and X_1^4 (with EG), X_2^4 (with 1,2PG), X_3^4 (with 1,3PG) and X_4^4 (with GL) degassed at 250°C. The following values of specific surface area, in [m^2 g^{-1}], were obtained: 27, for X_0^4; 360, for X_1^4; 420, for X_2^4; 460, for X_3^4 and 546, for X_4^4.

From these values of specific surface areas, we may conclude that the link of polyols inside the silica matrix leads to changes on the matrixes morphology, due, probably, to the modified pores diameter and pore size distribution. These aspects are still under study.

Conclusions

This study on the interaction of some polyols with TEOS and its hydrolysis products, provide that this polyols covalently bound through Si–O–C link in the silica network, forming hybrid matrixes. By thermal treatment of these hybrid matrixes, at temperatures above 300°C, silica matrixes with modified morphology are obtained, depending on the polyols nature and on the interaction mechanism of the polyol with the functional groups of the matrix.

The thermal analysis proves to be the most appropriate technique to evidence the organic chains linked in the matrix network, and to follow also the thermal evolution of the gels to the SiO_2 matrix.

Acknowledgements

This paper was supported from the CNCSIS A 648/2006 grant, by the programm MEdC, Romania.

References

1 T. Higuchi, K. Kuramada, S. Nagamine, A. W. Lothongkum and M. Tanigaki, J. Mater. Sci., 35 (2000) 3237.
2 O. Shilova, E. V. Tarasyuc, V. V. Shevchenko, N. S.Klimenko, T. G. Movchan, S. V. Hashkovsky and V. V. Shilov, Glass Phys. Chem., 29 (2003) 378.
3 D. Sternik, P. Staszczuk, J. Pekalska, G. Grodzicka, B. Gawdzik, J. Ospiuk-Tomasik and P. Witer, J. Therm. Anal. Cal., 86 (2006) 85.
4 N. N. Khimich, Glass Phys. Chem., 30 (2004) 430.
5 V. Castelvetro and Cinzia De Vita, Adv. Colloid Interface Sci., 108–109 (2004) 167.
6 M. Zaharescu, A. Jitianu, A. Braileanu, J. Madarász, Cs. Novák and G. Pokol, J. Therm. Anal. Cal., 71 (2003) 421.
7 M. Zaharescu, A. Jitianu, A. Braileanu, J. Madarász and G. Pokol, J. Therm. Anal. Cal., 64 (2001) 689.
8 C. L. Beaudry, L. C. Klein and R. A. McCauley, J. Thermal Anal., 46 (1996) 55.
9 R. F. S. Lenza and W. L. Wasconcelos, Mater. Res., 4 (2001) 175.
10 V. K. Parashar, V. Raman and O. P. Bahl, J. Mater. Sci. Lett., 15 (1996) 1403.
11 N. Uchida, N. Ishiyama, Z. Kato and K. Uematsu, J. Mater. Sci. Lett., 29 (1994) 5188.
12 C. P. Higginbotham, R. F. Browner, J. D. Jenkins and J. K. Rice, Mater. Lett., 57 (2003) 3970.
13 M. Laridjani, E. Lafontaine, J. P. Bayyl and P. Judeinstein, J. Mater. Sci., 34 (1999) 5945.
14 P. Ågren and J. B. Rosenhohn, J. Colloid Interface Sci., 204 (1998) 45.
15 A. V. Rao and M. M. Kulkarni, Mater. Chem. Phys., 77 (2003) 819.
16 G. M. Neves, R. F. S. Lenza and W. L. Vasconcelos, Mater. Res., 5 (2002) 447.
17 D. Ravanie, A. Seminel, Y. Charbouillot and M. A. Vincens, J. Non-Cryst. Solids, 82 (1986) 210.
18 M. Stefanescu, M. Stoia and O. Stefanescu, J. Sol-Gel Sci. Technol., (2006) in press.
19 M. Stefanescu, C. Caizer, M. Stoia and O. Stefanescu, Acta Mater., 54 (2006) 1249.
20 M. Stefanescu, C. Caizer, M. Stoia and O. Stefanescu, J. Optoelectron. Adv. Mater., 7 (2005) 607.
21 C. J. Brinker and G. V. Scherer, Sol-gel Science, Academic Press, San Diego 1990, p. 501.
22 F. Touati, N. Gharbi and H. Zarrouk, J. Sol-Gel Sci. Technol., 8 (1997) 595.
23 C. J. Brinker and G. V. Scherer, Sol-gel Science, Academic Press, San Diego 1990, p. 552.
24 V. Jitchum, S. Chivin, S. Wongkasemjit and H. Ishida, Tetrahedron, 57 (2001) 3997.
25 R. F. S. Lenza and W. L. Vasconcelos, J. Non-Cryst. Solids, 330 (2003) 216.
26 R. F. S. Lenza and W. L. Vasconcelos, Mater. Res., 4 (2001) 189.
27 Ch. Voulgaris, E. Amanatide, D. Mataras and D. E. Rapakoulies, J. Phys.: Conference Series, 10 (2005) 206.
28 G. M. Neves, R. F. S. Lenza and W. L. Vasconcelos, Mater. Res., 5 (2002) 447.
29 V. A. Maroni and S. J. Epperson, Vibr. Sperctrosc., 27 (2001) 43.

DOI: 10.1007/s10973-006-8002-7