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Rheological Studies of some Ethylene-Glycol – TEOS Gels

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Abstract: Hybrid organic-inorganic materials, silica – ethylene glycol (EG), were prepared by the sol-gel process from mixtures of tetraethoxisilane (TEOS) and EG under acidic catalysis. The resulting hybrid material was studied through thermal analysis and FT-IR spectroscopy. These techniques evidenced the presence of EG in the silica matrix chemically bonded (through condensation) in the silica network. The gels evolution during the gelation process was followed by means of the rheological behavior studies

Keywords: gelation time, sol-gel process, rheological behavior, viscoplastic

1. Introduction

The design of hybrid (organic-inorganic) nanocomposites is of great interest for science and technology. Many applications of these are in view for the future, in fields such as optical materials, mechanics, iono-electronics, biosensors, membranes [1,2]. Practically, inorganic precursors (alkoxides of silica) and organic polymers (most frequently polyethylene glycol and polyvinyl alcohol) are mixed to obtain a "hybrid" solid matrix using hydrolysis-condensation under various catalytic conditions. These hybrid materials were studied through various techniques in order to determine their morphology and porous structure [3].

Adding organic additives to the TEOS-H_2O system in the initial phase (sol) influences both the hydrolysis and the condensation process and leads to the gel structure (matrix) modification [4]. In the current literature, the effect of organic additives (ethylene glycol [5], glycerol [6], formaldehyde [4], poly ethylene glycol [3]) on the gelling process (hydrolysis and condensation) is explained mostly by the formation of hydrogen bonds both with water and the ≡Si-OH groups.

In our previous studies we have evidenced that EG chemically bond in the silica network, by condensation with the silanol groups (Si – OH), formed hybrid ethylene glycol – silica matrix [7].

In this paper we present the study of ethylene glycol (EG)-TEOS gels synthesized in acidic catalysis, by means of rheology, in order to evidence the interaction between EG and the hydrolysis products of TEOS during the geling process.

2. Materials and methods

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

The sols synthesis was performed at room temperature, under continuous magnetic stirring of the TEOS-ethanol solution which was added to the hydroalcoholic solution of EG, previously acidulated with HNO_3 (c_{ac}=0.001 mol/L). After 30 minutes of stirring, a clear solution was obtained. This solution was left to gel at room temperature. Periodically, it were prelevated samples from these sols (at first), than gels (G1), in order to perform rheological study. We have also synthesized a gel without EG (G0).

The obtained gels were dried at 65°C for 10 hours, than thermally treated at 200°C, in order to be studied by FT-IR and thermal analysis.

Experimental techniques:

- differential thermal analysis (DTA), thermogravimetry (TG) with 1500 D MOM Budapest Derivatograph, 20÷500°C, 5°C/min, α-Al_2O_3 as inert material, Pt crucibles in the form of plates;
- FT-IR spectroscopy with a JASCO 430 FT-IR spectrometer, in a KBr pellet, in the range 400÷4000 nm;
- measurement of the specific surface with MICROMERITICS ASAP 2000;
- using the rotational viscometer Rheotest-2 is measured the shear stress which are developed into a fluid placed into the ring-shaped space of two coaxial cylinders. One of them (inner) executes controlled rotational motions. From the correlation between the shear stress and the shear rate $\tau = f(\gamma)$ was established the rheological behavior of these gels.

3. Results and discussion

The silica-gel obtaining process involves the hydrolysis of TEOS (1) and the condensation of hydrolysis products with elimination of water (2) or alcohol (3), depending on the H_2O/TEOS ratio:

$$\equiv Si - OR + H_2O \Leftrightarrow \equiv Si - OH + ROH \quad (1)$$

$$\equiv Si - OH + HO - Si \equiv \; \Leftrightarrow \; \equiv Si - O - Si \equiv + H_2O \quad (2)$$

$$\equiv Si - OR + HO - Si \equiv \; \Leftrightarrow \; \equiv Si - O - Si \equiv + ROH \quad (3)$$

For the TEOS-EG-H_2O system, our previous studies for a molar ratio 1:1:4, have shown that in the process of matrix formation, EG interacts chemically with the silanol groups, finally forming a hybrid matrix, in which the organic chain is bounded with the Si atom through Si-O-C covalent bounds [7]:

$$\text{Si-OH} + \text{HO-CH}_2\text{-CH}_2\text{-OH} \rightleftharpoons \text{Si-O-CH}_2\text{-CH}_2\text{-OH} + H_2O \quad (4)$$

$$\text{Si-O-CH}_2\text{-CH}_2\text{-OH} + \text{HO-Si} \rightleftharpoons \text{Si-O-CH}_2\text{-CH}_2\text{-O-Si} + H_2O \quad (5)$$

Both gel types were studied by thermal analysis and FT-IR spectrometry.

In figure 1 are presented the TG and DTA curves obtained at thermal analysis, in air, until 500˚C, for the gels synthesized with EG (G1) and thermally treated at 200˚C.

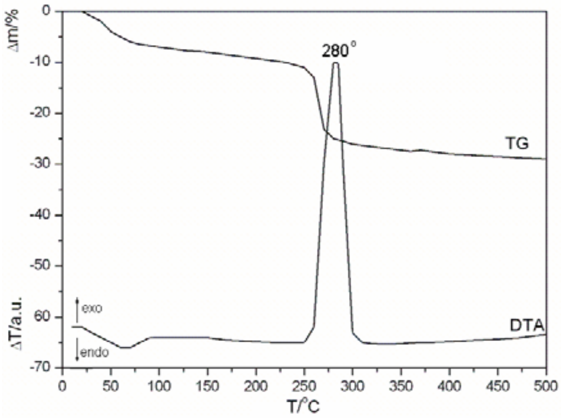

Figure 1. Thermal analysis for gels synthesized with EG (G1)

The process with mass loss, in the temperature range 250÷350˚C, is attributed to the oxidative decomposition of the organic chains corresponding to the polyols interspersed in the silica matrix, process 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÷1000˚C range, the slow mass loss can be attributed to the polycondensation reactions promotion, the final residue presenting a yellowish colour due to the residual products resulted from the combustion process of the organic part from the matrix.

In case of gel G0, no exothermic heat effect was evidenced on the DTA curve.

Figure 2 presents the FT-IR spectra of the gels G0 (without EG) and G1 (with EG).

Spectrum (1) for gel G0 presents the absorption bands characteristic to the silica matrix: at 480 cm^{-1} attributed to the vibrations of the Si-O bond, a shoulder at 580 cm^{-1} attributed by some authors to cyclic Si-O-Si structures, at 798 cm^{-1} attributed to the SiO_4 tetrahedron, at 945 cm^{-1} attributed to the Si-OH groups and at 1080 cm^{-1} with a shoulder at 1200 cm^{-1} attributed to the bond stretching vibrations of Si-O-Si. The band at 1650 cm^{-1} is attributed to the deformation vibrations of the H-O-H bond, which indicates the presence of water incorporated in the silica matrix. The wide band with a minimum in the range 3400÷3500 cm^{-1} is attributed to the –OH groups in water and in the matrix.

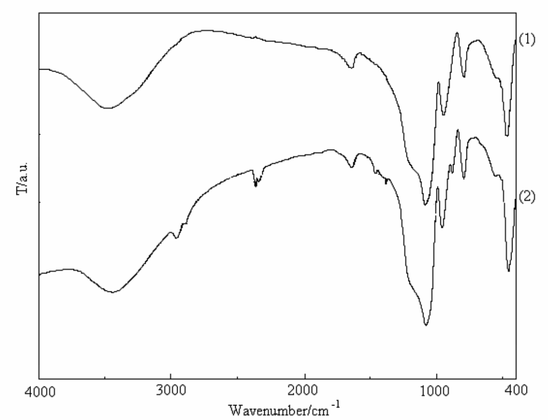

Figure 2. FT-IR spectra of the gels G0 (without EG) and G1 (with EG)

The spectrum (2) of gel G1 with ethylene glycol not only displays the bands characteristic to the silica matrix, but also a series of bands that are caused by the presence of EG. Thus, bands characteristic to the C-H bond appear in the ranges 2800÷3000 cm^{-1} and 1400÷1500 cm^{-1}, which are attributed to the -CH_2- groups in free ethylene glycol or bonded in the matrix. There is also the band at 880 cm^{-1} that is characteristic to the deformation vibrations of the C-C bond in EG [8].

In order to observe the effect of EG on the morphology of the silica matrix, we have determined the specific surface of samples G0 and G1 thermally treated at 280°C for 3 hours. For G0, a specific surface of 27m^2/g was obtained and for G1, the specific surface was 360 m^2/g. This demonstrates a significant influence of ethylene glycol on the porous structure of the silica matrix.

Rheological investigations have followed the influence of a) the type and the length of preservation and b) the temperature, about G0 and G1 gels. Gels preservation between two experimental measurements was done a) in an uncover glass or b) in the space between the inner mobile cylinder and the fixed outer cylinder of the Rheotest-2 rotational viscometer, at room temperature. The measurements were done under temperature control. The dependence of the shear stress τ as a function of the shear rate γ is shown in figure 3 for G1 gel and in figure 4 for G0 gel.

For both gels, the $\tau = f(\gamma)$ dependence type is $\tau = \tau_0 + K \cdot \gamma^m$, and their behavior is characteristic to viscoplastic liquids ($\tau_0 \neq 0; m = 1$) [9-11], Table 1.

TABLE 1. The values of initial shear stress τ_0 and of preexponential coefficient K for G1 and G0 gels (t_1 = 22˚C)

Time, hours	G1		G0	
	τ_0, Pa	K	τ_0, Pa	K
0	1.239	0.0062	1.184	0.0062
48	2.091	0.0256	1.487	0.0069
72	2.632	0.0536	1.553	0.0087
96	33.847	0.2103	1.642	0.0148
144	-	-	22.26	0.2869

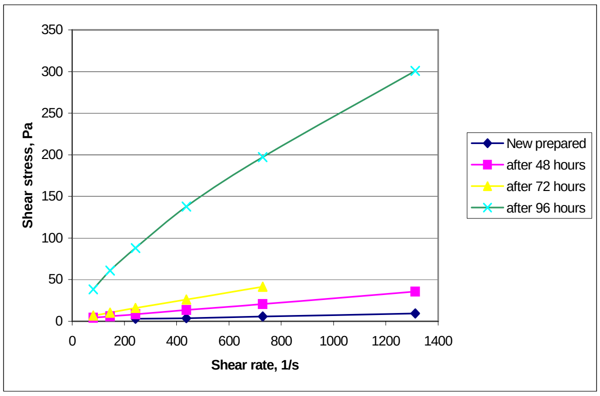

Figure 3. Shear stress versus shear rate for G1 gel (preservation in uncover glass, t1 = 22˚C)

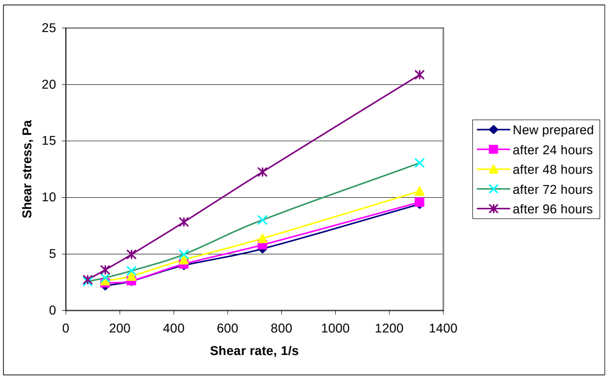

Figure 4. Shear stress versus shear rate for G0 gel (preservation in uncover glass, t1 = 22˚C)

From the slope of $\tau = f(\gamma)$ lines were established the apparent viscosity values and their time dependence is shown in figure 5.

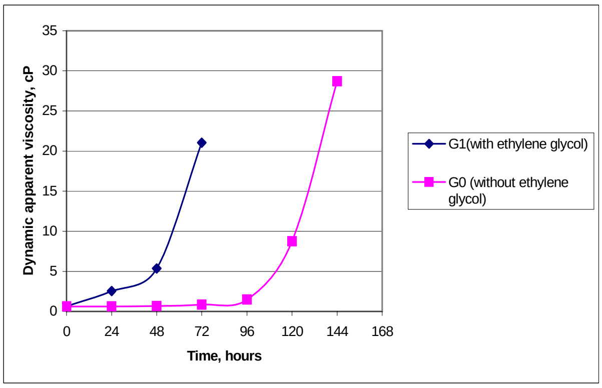

Figure 5. Time dependence of the apparent viscosity (preservation in uncover glass, t1 = 22˚C)

We mainly observe, on the one hand, that the gel with ethylene glycol (G1) has bigger values of the apparent viscosity in time, respectively, it reaches faster the gelation time (the moment until the shear stress measurement is possible) in comparison with G0 gel (without ethylene glycol).

The same observations are valid for G1 gel also in the case when it is preserved into an uncover glass in comparison with the case when it is preserved in the measure space of the rheometer, figure 6.

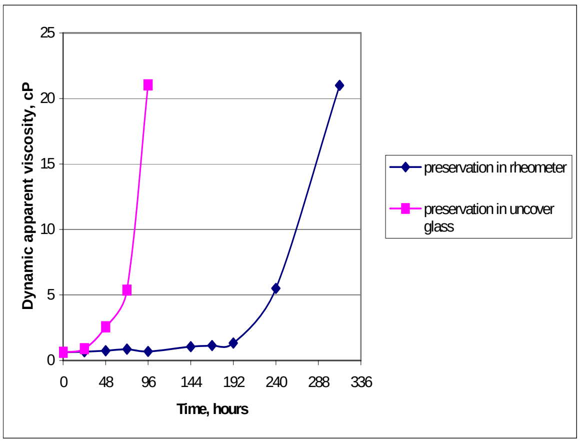

Figure 6. Evolution of apparent viscosity versus time as a function of preservation type (G1 gel, t_1 = 22˚C)

Viscoplastic behavior of both gels is also maintained to temperature increasing (t_2 = 40˚C) and preservation in rheometer, Table 2.

In these conditions, the dependence of apparent viscosity in time for the two gel types is shown in figure 7a, b.

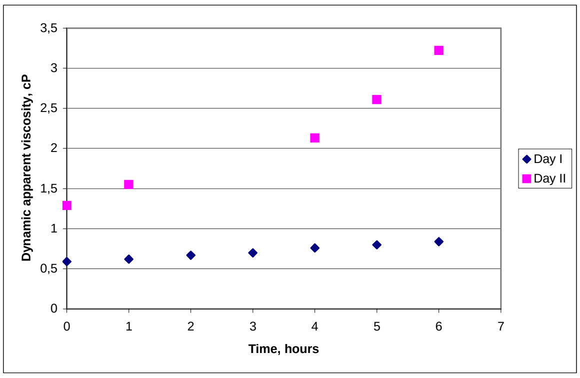

Figure 7a. Evolution in time of apparent viscosity (G1 gel, t2 = 40˚C)

TABLE 2. The values of initial shear stress τ_0 and of preexponential coefficient K for G1 and G0 gels (t_2 = 40˚C)

Day	Time, hours	G1		G0	
		τ_0, Pa	K	τ_0, Pa	K
I	0	1.383	0.0059	1.734	0.0042
	1	1.635	0.0062	1.643	0.0044
	2	1.744	0.0067	1.506	0.0049
	3	1.759	0.0070	1.485	0.0054
	4	1.580	0.0076	1.377	0.0060
	5	1.693	0.0080	1.340	0.0064
II	0	1.445	0.0129	1.491	0.0109
	1	1.654	0.0155	1.523	0.0127
	4	1.777	0.0213	1.641	0.0337
	5	1.898	0.0261	1.986	0.0551
	6	2.243	0.0322	-	0.0918
	7	-	-	-	0.1610
III	0	149.94	0.302	-	-

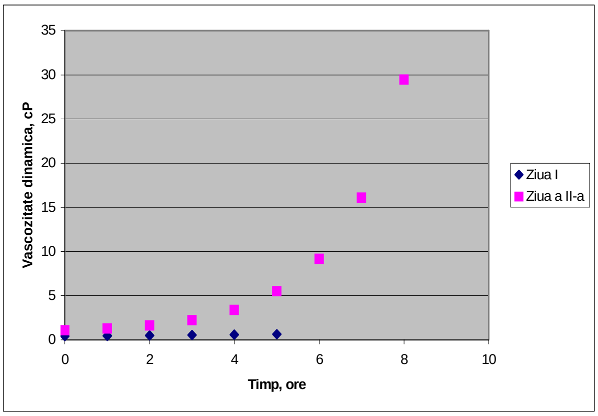

Figure 7b. Evolution in time of apparent viscosity (G0 gel, t2 = 40˚C)

4. Conclusions

- both gels (with and without ethylene glycol) have a viscoplastic behavior with rheological equation $\tau = \tau_0 + K \cdot \gamma$;

- at room temperature and samples preservation in uncover glasses, G1 gel has bigger values of the apparent viscosity in comparison with G0 gel. Also, the gelation time for G1 gel is faster (~ 96 hours) than for G0 gel (~ 144 hours);

- the preservation of G1 gel in uncover glass at room temperature leads to a faster increasing of apparent viscosity and, implicit, to a shorter gelation time (96 hours in comparison with 288 hours for preservation in rheometer);

- the temperature increasing caused initially a liniar dependence between the apparent viscosity and time for both gels.

After 20 hours preservation and new measurements in the same conditions, the viscosity measurements in the same conditions, the viscosity increasing is exponentially.

Until a certain moment, G1 gel has a bigger apparent viscosity than G0. After that appears an unexpected increasing of G0 gel consistency and a faster gelation time (30 hours in comparison with 55 hours for the gel with ethylene glycol). The phenomenon can be explained through the formation of a tridimensional structure, more compact and more rigid, with ≡Si-O-Si≡ bonds, in the case of gel without ehylene glycol.

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