



SYNTHESIS AND CHARACTERIZATION OF POLY(VINYL ALCOHOL)/ETHYLENE GLYCOL /SILICA HYBRIDS. THERMAL ANALYSIS AND FT-IR STUDY

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Received October 2, 2008

In the present work, poly(vinyl alcohol)(PVA)/tetraethylortosilicate (TEOS) hybrids and poly(vinyl alcohol)(PVA)/ tetraethylortosilicate (TEOS)/ethylene glycol(EG) were synthesized by the sol/gel process. Hybrids gels EG/TEOS and PVA/EG and simple PVA and TEOS gels were also synthesized. The thermal analysis of the gels has evidenced that EG interacts both with partially hydrolyzed siloxane and with PVA during the formation of the hybrid gels. FT-IR spectra of the hybrids have showed major vibration bands associated with organic-inorganic chemical groups presented in the hybrids PVA/TEOS and PVA/TEOS/EG systems. By thermal decomposition of the PVA/EG/TEOS hybrids we have obtained silica matrices with modified morphology, evidenced by SEM images.

INTRODUCTION

In the last decade sol-gel method was widely used for the synthesis of hybrid organic-inorganic materials. The preparation of hybrid organic-inorganic composites has attracted much attention because such hybrids may show controllable physical properties, such as optical, electrical and mechanical behaviors.¹ These hybrids combine the properties of organic polymers with the properties of ceramics. The components of the hybrids can be mixed at length scale, ranging from the nanometer to micrometer, theoretically in any ratio.² The final bulk properties of the hybrid organic-inorganic composites synthesized by the sol-gel method depend on the homogeneity of the sol-gel mixture.

PVA/silica system has attracted recent attention due to the hydrogel behavior of polyvinyl alcohol. PVA is a synthetic water soluble hydrophilic polymer. The basic properties of PVA depend on the degree of polymerization or on the degree of

hydrolysis. The PVA-silica hybrids have been prepared by sol-gel methods, starting from tetra(ethyl)ortosilicate³ or tetra(methyl)ortosilicate⁴ and PVA and were characterized for potential applications in drug delivery, selective membranes or immobilization of carriers for biocatalyst.⁵ PVA must be cross-linked in order to be useful for a wide variety of applications. Some of the common cross-linking agents used for PVA hydrogel preparation include dimethyl sulfoxide (DMSO), glutaraldehyde², acetaldehyde and sulfosuccinic acid.⁴

In this paper we report the synthesis and characterization of PVA/EG/TEOS hybrid gels, starting from tetraethylortosilicate and poly(vinylalcohol), in the presence of ethylene glycol. Our previous studies have shown that ethylene glycol chemically interact with Si-OH during gelation and thermal treatment of the TEOS-EG-H₂O gels. The result, after annealing of the hybrid gels, is the formation of silica matrices with modified morphology.^{5,6} The introduction of

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PVA in the TEOS-EG system may lead to homogeneous organic-inorganic hybrids, with specific properties, suitable for obtaining of quality thin films.

The obtained composites have been characterized by thermal analysis, FT-IR study and SEM, in order to evidence the nature of the interaction between silica and PVA and the influence of EG.

RESULTS

All synthesized gels (see table 1) have been characterised by FT-IR spectrometry and thermal analysis in order to evidence the possible interaction between PVA and TEOS and between

PVA and EG during the formation of the hybrids TEOS/PVA and TEOS/EG/PVA, with different PVA content.

Fig. 1 presents the FTIR spectra of gels P (1), T (2) and TP with different PVA content ((3) and (4)), while fig. 2 presents the FTIR spectra of EG(1) and gels TE(2) and TPE with different PVA content ((3) and (4)).

All gels have been characterized by thermal analysis, by heating in air (static atmosphere), with a heating rate of 10 degree/min, until 800°C. Figure 3 presents the DTA curve obtained for the gels T(1) and TE(2), while figure 4 presents the DTA curve of the gels P(1) and PE(2).

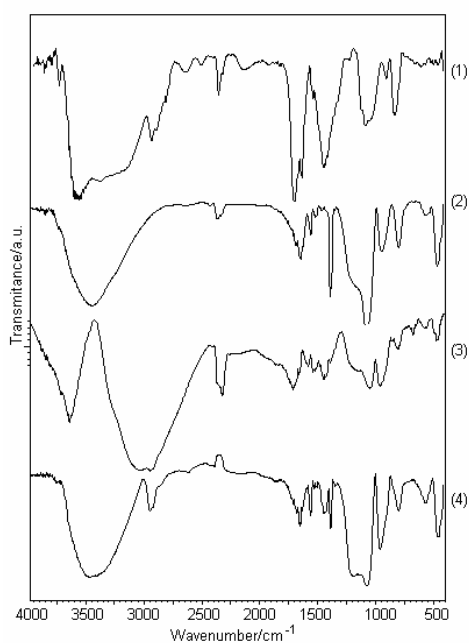


Fig. 1 – FTIR spectra of gels P(1), T(2), TP2(3), TP4(4) dried at 40°C.

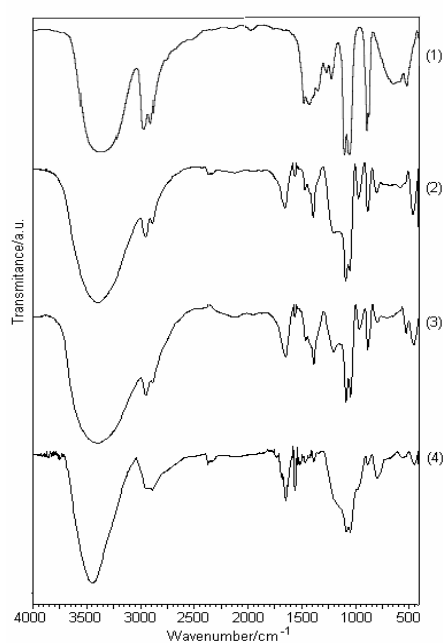


Fig. 2 – FTIR spectra of EG (1) and of gels TE(2), TPE2(3), TPE4(4), dried at 40°C.

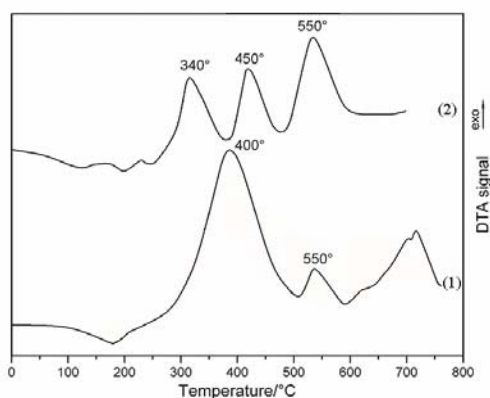


Fig. 3 – DTA curves of gel T(1), TE(2), dried at 40°C.

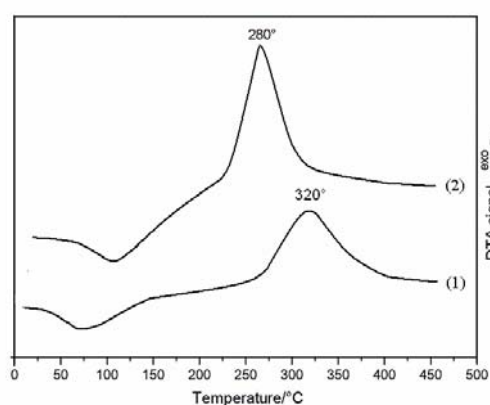


Fig. 4 – DTA curves of gel P(1) and PE(2), dried at 40°C.

The thermal behaviour of the hybrid gels TP and TPE, with different PVA content was studied by heating in air (static atmosphere) until 600°C.

The obtained thermal curves (TG, DTG, DTA) for the gels TP3 and TPE3 are presented in fig. 5 and fig. 6.

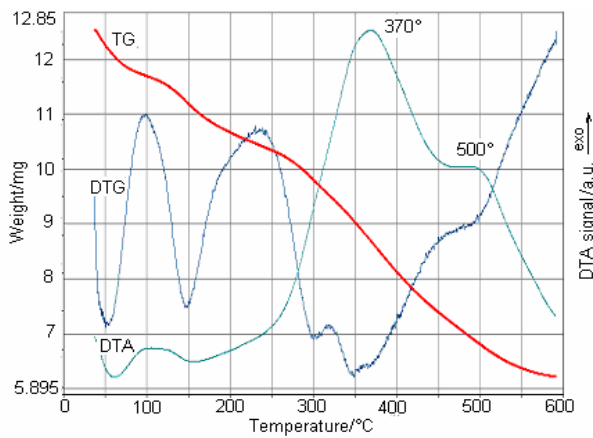


Fig. 6 – Derivatogram of the gel TPE3, dried at 80°C.

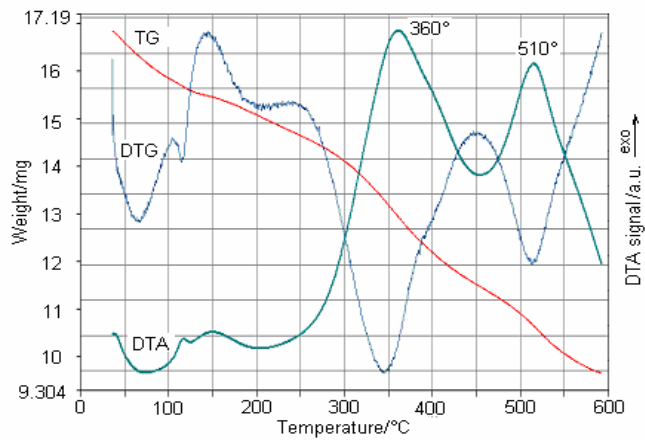


Fig. 5 – Derivatogram of gel the gel TP3, dried at 80°C.

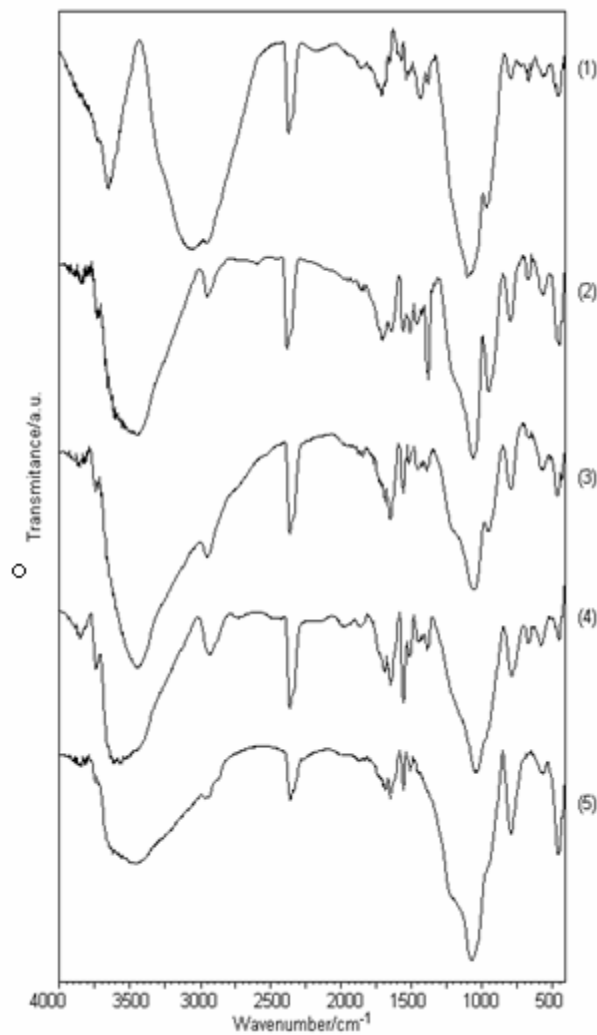


Fig. 7 – FTIR spectra of gel TP3 thermally treated at: 40°C (1), 80°C (2), 200°C (3), 300°C (4) and 400°C (5).

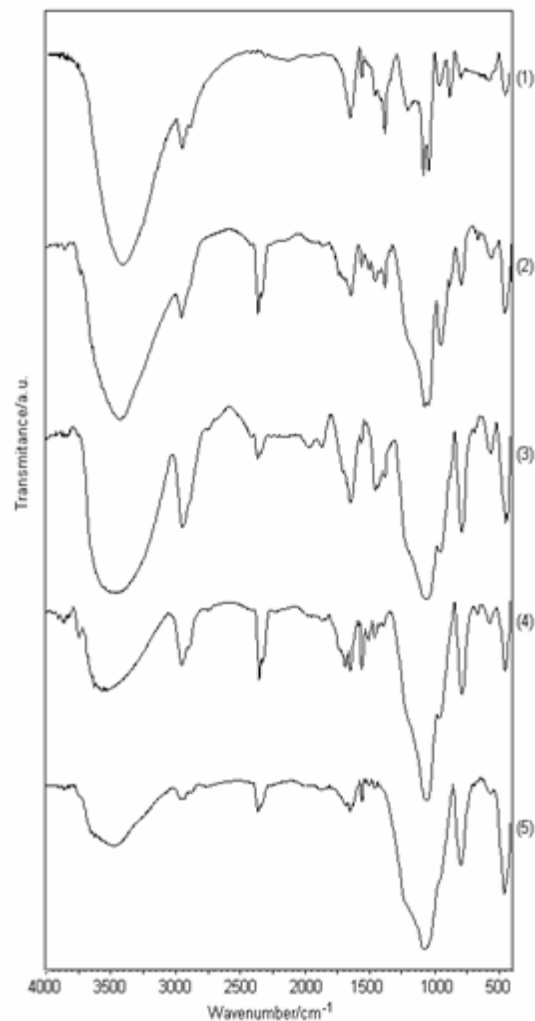


Fig. 8 – FTIR spectra of gel TPE3 thermally treated at: 40°C (1), 80°C (2), 200°C (3), 300°C (4) and 400°C (5).

The evolution of the hybrids TP3 and TPE3 with the temperatures was also studied by FTIR spectrometry. The spectra of the hybrid gels TP and TPE thermally treated at 40°C, 80°C, 200°C, 300°C and 400°C are presented in the fig. 7(TP3) and fig. 8 (TPE3).

The SEM image of the silica matrix obtained by annealing the hybrid gel TPE3 at 600°C is presented in fig. 9.

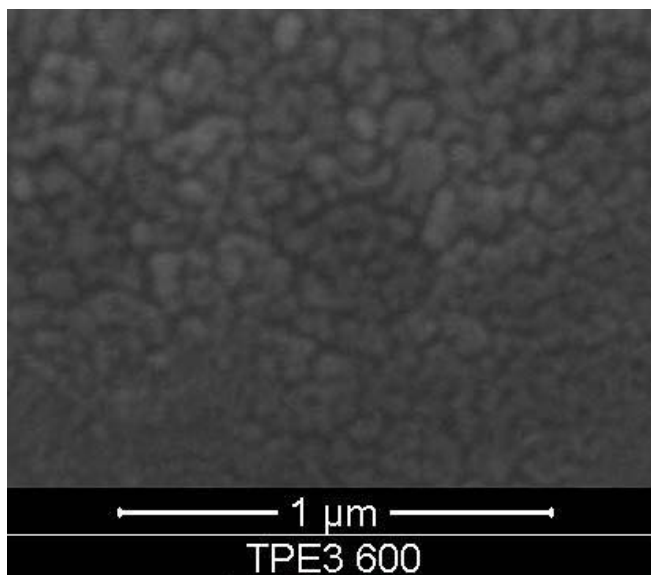


Fig. 9 – SEM image of the silica matrix obtained by annealing the gel TPE3 at 600°C.

DISCUSSION

The studies reported in the literature^{4,7} have pointed out that acidic catalysis facilitates the formation of hybrids TEOS/PVA, due to the extensive H-bonding between the polymer and silica network and to the crosslinking of these two polymers by polycondensation reactions, enabling system homogeneity.

In our previous studies^{5,6} we showed that the presence of ethylene glycol in the TEOS-H₂O system leads to homogeneous hybrid gels due to the chemical interaction between EG and silica. The presence of EG facilitates the formation (after a suitable thermal treatment) of silica matrices with modified morphology (higher specific surface areas).

We initiated the present study of TEOS-PVA-EG gels in order to establish the possible interactions between EG and PVA that might influence the formation of the hybrid gels TEOS/PVA/EG, for later applications in thin silica films with high specific surface area.

Fig. 1 presents the FT-IR spectra of PVA hydrogel (P), silica gel (T) and TEOS/PVA hybrid gels (TP2, TP4) obtained at room temperature.

Spectrum (1) of the PVA hydrogel (P) presents bands characteristic to free (3560 cm⁻¹) and

hydrogen bonded (3157 cm⁻¹) -OH groups², to CH₂ and CH groups (2933 cm⁻¹, 2860 cm⁻¹, 1346 cm⁻¹)^{8,9} and to C – O stretching of free and condensed C-OH groups (1440 cm⁻¹, 1099 cm⁻¹ and 840 cm⁻¹).^{2,10} It also presents bands characteristic to terminal vinyl groups⁵ (1660 cm⁻¹) and non-hydrolyzed vinyl acetate groups (band at 1720 cm⁻¹)⁸ from PVA.

Spectrum (2) of silica gel (T) displays bands characteristic to H-bonded -OH (Si-OH and H-OH) at 3430 cm⁻¹ and 1640 cm⁻¹ and bands characteristic to the Si – O – Si bonds¹⁰ at 1074 cm⁻¹, 798 cm⁻¹ and 462 cm⁻¹. The band at 952 cm⁻¹ is due to the Si – OH stretching vibrations.¹

Spectra (3) and (4) of the hybrid gel TEOS/PVA: TP2 (spectrum 3) and TP4 (spectrum 4) display bands characteristic both to silica matrix (455, 567 cm⁻¹, 798, 960, 1072, 1649) and to PVA (3200-3400 cm⁻¹, 2945 cm⁻¹, 2890 cm⁻¹, 1556 cm⁻¹, 1438 cm⁻¹, 1130 cm⁻¹), partially overlapped. Comparison of the IR spectra obtained for TEOS/PVA gels with different contents of PVA showed that for initial molar ratio PVA (expressed in mole of [C-C] units)/TEOS lower than 1.33 (e.g. TP2 (spectrum 3)), a strong band is present at ~3600 cm⁻¹, due to the unassociated -OH groups (from PVA). In these cases another band appears at

3100-3200 cm^{-1} , attributed in literature¹¹ to the intramolecular H-bonded hydroxyl groups, but also to the H-bonded hydroxyl group having polymeric association. This may be explained by some phase separation in the hybrids, reported in literature for high TEOS content in the gels.¹² For an initial PVA (expressed in mole of [C-C] units)/TEOS molar ratio of 1.33 (TP4 - spectrum (4)), a broad band appear in the range 3300-3500 cm^{-1} due to the H-bonded -OH groups.

In the FTIR spectra of the TP gels the band from 960 cm^{-1} characteristic to Si-OH groups is strong, while the band from ~ 800 cm^{-1} characteristic to the Si-O-Si symmetric stretching is weak, indicating a low degree of polycondensation of silica network.¹⁴ The increased intensity of the band at 567 cm^{-1} which can be assigned to Si-O-Si ring structure,¹³ indicates the formation of such silica clusters.

In order to facilitate the formation of continue organic (PVA) phase within the silica matrix and to enhance the homogeneity of the hybrid material, we have introduced ethylene glycol in the TEOS/PVA system. Figure 2 presents the FT-IR spectra of EG (spectrum 1), of the gels TEOS/EG (TE) (spectrum 2) and TEOS/EG/PVA with different PVA content: TPE2 (spectrum 3) and TPE4 (spectrum 4).

Spectrum (1) of pure ethylene glycol exhibits the bands characteristic to associated and free C-OH groups (3400 cm^{-1} , 1100-900 cm^{-1} , 530 cm^{-1}), to CH₂ groups (2800-3000 cm^{-1} , 1300-1400 cm^{-1}) and to C-C bonds (880 cm^{-1}). Spectrum (2) of the gel TE shows beside the bands characteristic to silica matrix, some bands characteristic to ethylene glycol (2951, 2885, 1460, 1083, 1043, 881 cm^{-1}). The addition of PVA in TEOS/EG system produces minor modifications in the FT-IR spectrum, regarding the relative intensities of some bands. The band from 1200 cm^{-1} attributed to Si-O-C bonds and also to C-O-C bonds indicates the formation of hybride organic inorganic structures, due to the interaction of EG and PVA with the Si-OH groups. The absence of the band from 1440 cm^{-1} characteristic to C-OH groups from PVA indicates a high degree of condensation (self-condensation and condensation with EG).

All gels have been analyzed by thermal analysis (TG, DTA) in air up to 800°C, in order to study their thermal behaviors and to evidence the interaction between hybrids' components.

Fig. 3 presents the DTA curves of the gels T and TE dried at 40°C. DTA (1) curve of gel T presents an endothermic effect corresponding to the elimination of volatils (H₂O, C₂H₅OH). The exothermal effect with maximum at 320°C correspond to the burning of the residual (-OC₂H₅) groups. DTA (2) of the gel TE (TEOS/EG)

presents a stronger exothermic effect at 280°C due to the burning of the organic chains resulted by the chemical interaction of EG with Si-OH groups^{5,6}.

Fig.4. presents the DTA curve of the gels P (PVA) – DTA (1) and PE (PVA/EG) – DTA (2).

The thermal behaviour of PVA gel was in agreement with the literature data¹⁵⁻¹⁷. The decomposition of PVA gel (DTA 1) takes place in the range 300-600°C with two exothermic steps, leaving a carbonaceous residue that burns around 700°C. The thermal degradation of PE gel takes place in three comparable exothermic steps, the decomposition being complete at 600°C (no residual mass). The strong exothermic effect around 550°C was related in literature¹⁸ with the crosslinking of PVA. In our case the crosslinking is due to the presence of EG (OH-CH₂-CH₂-OH) that can interact with PVA forming ether type bonds. This interaction leads to multiple -O-CH₂-CH₂-O- bridge between PVA chains -[CH₂-CH(O-)]_n-. Due to the cross-linking of PVA chains by EG few C-OH groups remains unbounded, thus few double bonds form by dehydration, so that the thermal decomposition of the gel is different and finishes at lower temperature compared with the PVA gel (P).

The thermal behavior of the hybrid gel TP3 (TEOS/PVA) is shown in fig. 5. From the thermal curves evolution results that adsorbed water is lost until 100°C, than there is a slow mass loss in the range 100°C-300°C due to the on going polycondensation reaction of the silica matrix and also of PVA with Si-OH groups. The thermal degradation of the organic fraction (PVA, -OC₂H₅) takes place in the range 300°C-600°C, where two exothermal corresponding effects are registered on the DTA curve, similar to the PVA degradation DTA curve (fig.4, DTA (1)). The residue at 600°C is black, so residual carbon is present.

In case of the gel TPE3 with EG (fig. 6) a supplementary mass loss takes place in the range 100 – 200°C due to the volatilization of unbounded EG from the pores. The corresponding mass loss in this range decrease with the increasing in PVA content, suggesting that chemical interaction takes place between EG and PVA, decreasing the content of free EG. The thermal degradation of the organics (PVA, bounded EG by condensation with C-OH and Si-OH groups) takes place in the range 250°-600°C. The strong exothermal effect with maximum at 370°C is due mainly to the thermal degradation of (-CH₂-CH₂-) chains resulted from the interaction of EG with silica matrix and with PVA, and partially to PVA degradation. The exothermal effect from 500°C increases with the increase of PVA content, so it is related with PVA

thermal degradation. The residue at 600°C is white, so we have no residual carbon left in this case.

The evolution of the hybrid gels with the temperature was studied also by FT-IR spectrometry. Fig. 7 and Fig. 8 present the FT-IR spectra of the gels TP3 (fig.7) and TPE3 (fig.8) thermally treated at 40, 80, 200, 300 and 400°C.

In case of the gel TP3 (fig. 7) modifications of FTIR spectra with the temperature of the thermal treatment occur first in the 3000-4000 cm^{-1} range. Thus, by heating the gel at 80°C the band characteristic to non-bonded C-OH groups (3600 cm^{-1} , spectrum 1) significantly diminishes, while the band characteristic to H-bounded -OH groups becomes a broad band in the range 3000-3500 cm^{-1} (spectrum 2). Also, starting with 80°C (spectrum 2) but more obvious at 200°C (spectrum 3), new bands appear at 1700 cm^{-1} and 1570 cm^{-1} , due to the double bonds (C=C) generated by dehydration of unbounded C-OH groups of PVA and possible to some C=O bonds¹⁵ formed during PVA decomposition. These bands together with the bands characteristic to C-H bonds (1300-1400 cm^{-1} , 2800-3000 cm^{-1}) are also present in the spectrum (4) of the gel treated at 300°C, but become weak at 400°C (spectrum 5).

In case of the gel TPE3 (TEOS/PVA/EG), the evolution of FTIR spectra with the temperature of the thermal treatment is different (fig.8). Thus, in the region 3000-3500 cm^{-1} no differences appears, but a decrease in intensity of the band from 3400 cm^{-1} at temperature higher than 200°C (spectra 4 and 5). Spectra (1) and (2) present the band from 880 cm^{-1} characteristic to EG, but at 200°C (spectrum 3) the band characteristic to EG become less visible, due to its volatilization from the matrices pores. Only the EG bounded with Si-OH

or C-OH groups remains in the gel above 200°C. The bands characteristic to C-H bonds (1300-1400 cm^{-1} , 2800-3000 cm^{-1}) are significantly weaker after thermal treatment at 400°C.

A significant aspect in case of the TPE3 gel is the higher intensity of the bands characteristic to silica matrix (especially 800 cm^{-1} and 460 cm^{-1}) starting from 200°C which reflects a more homogenous organic – inorganic hybrid in this case. A possible explanation is that EG interacts (by condensation) with both C-OH and Si-OH groups, playing the role of a cross-linking agent.

The SEM image of the silica matrix obtained after annealing of the gel TPE3 at 600°C is presented in fig.9. The SEM image of this sample evidenced the formation of a silica matrix with a homogenous structure and network-like porous structures resulted by thermal decomposition of the organic component of the initial hybrid gel.

EXPERIMENTAL

Tetraethylortosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS, > 99.5%), ethylene glycol (OH-CH₂-CH₂-OH) (> 99.5%) and PVA with an average molecular weight of 75 000 g/mol (hydrolysis degree >98%) were supplied by Merck.

5% (wt.%) PVA solution was prepared by dissolving PVA in distilled water and vigorously stirred at 60°C, using a magnetic stirrer. After total dissolution of the polymer HNO₃ was added to the solution. The 5% PVA solution was used for synthesis of PVA, PVA-EG hydrogels and of PVA/TEOS, PVA/EG/TEOS hybrids. The hybrids have been prepared by adding the corresponding mass of the PVA solution to the TEOS-H₂O-EtOH (for the PVA/TEOS hybrids) or to the TEOS-H₂O-EG-EtOH solution (for the PVA/EG/TEOS hybrids) under vigorous stirring with a magnetic stirrer. The molar ratio of the reactants for each sample are presented in table 1.

Table 1

Molar ratio of the starting materials for the gels synthesis

Sample	Quantity/mole				H ₂ O	Molar ratio TEOS:EG:PVA([C-C]):H ₂ O
	TEOS	EG	PVA			
			PVA	[C-C] unit		
P	-	-	1.33.10 ⁻⁵	0.0227	1.11	0:0:1:49
PE	-	0.0166	1.33.10 ⁻⁵	0.0227	1.11	0:3:4:195
TP1	0.0166	-	3.33.10 ⁻⁶	0.00568	1.11	3:0:1:195
TP2	0.0166	-	6.66.10 ⁻⁶	0.0114	1.11	3:0:2:195
TP3	0.0166	-	9.99.10 ⁻⁶	0.0170	1.11	3:0:3:195
TP4	0.0166	-	1.33.10 ⁻⁵	0.0227	1.11	3:0:4:195
TPE1	0.0166	0.0166	3.33.10 ⁻⁶	0.00568	1.11	3:3:1:195
TPE2	0.0166	0.0166	6.66.10 ⁻⁶	0.0114	1.11	3:3:2:195
TPE3	0.0166	0.0166	9.99.10 ⁻⁶	0.0170	1.11	3:3:3:195
TPE4	0.0166	0.0166	1.33.10 ⁻⁵	0.0227	1.11	3:3:4:195
TE	0.0166	0.0166	-	-	1.11	3:3:0:195
T	0.0166	-	-	-	0.11	3:0:0:19.5

The as obtained sols, have been left to gel at room temperature in covered recipients. After gelation, the obtained hybrids have been characterized by thermal analysis, FT-IR spectrometry and SEM microscopy.

Experimental techniques

The synthesized gels were characterized by thermal analysis using a 1500 D MOM Budapest derivatograph and a Diamond Perkin Elmer Termobalance. The experiments have been done in air, in the temperature range 20-800 °C, with a heating rate of 10 °C·min⁻¹, using as reference α -Al₂O₃. FT-IR spectrometry was performed with a Shimadzu Prestige-21 FT-IR spectrometer, in KBr pellets, in the range 400- 4000 cm⁻¹.

SEM images have been recorded with an Inspect-S microscope.

CONCLUSIONS

The presented study has evidenced that the introduction of PVA in TEOS/EG system leads to hybrid gels, more homogenous compared with TEOS/PVA hybrids. The interactions between EG-TEOS and EG-PVA have been evidenced by thermal analysis and FT-IR spectrometry.

The influences of the EG on the formation of the organic-inorganic hybrids and of the final silica matrix, suggests that he may play the role of a crosslinking agent.

REFERENCES

1. D.S. Kim, H.B.Park, J.W. Rhim and Y.M. Lee, *J. Membr. Sci.*, **2004**, *240*, 37-48.
2. E.F. dos Reis, F.S. Campos, A.P.Lage, R.C. Leite, L.G. Heneine, W.L. Vasconcelos, Z.I.P. Lobato and H.S. Mansur, *Mat. Res.*, **2006**, *9*, 158-191.
3. Kim, Y.liu, H. Chen, L. Zhang and X. Yao, *J.Sol-Gel Sci. Techn.*, **2002**, *25*, 95-101.
4. M. Cajlakovic, A. Lobnik T. and Werner, *Anal. Chim. Acta*, **2002**, *455*, 207-213.
5. M. Ștefănescu, M.Stoia and O. Ștefănescu, *J. Sol-Gel Sci. Techn.*, **2007**, *41*, 71-78.
6. M. Ștefănescu, M. Stoia, O.Ștefănescu, A.Popa, M.Simon and C. Ionescu, *J.Therm.Anal.Cal.*, **2007**, *88*, 19-26.
7. T. Kotoky and S.K. Dolui, *J. Sol-Gel Sci. Technol.*, **2004**, *29*, 107-114.
8. J.M. Gohil and A. Bhattacharya, P. Ray, *J. Polymer Res.*, **2006**, *13*, 161-169.
9. N.V. Petrova, A.M. Evtushenko, I.P. Chikhacheva, V.P. Zubov,I.V. and Kubrakova, *Russ. J. Appl. Chem.*, **2005**, *78*, 1158-1161.
10. B. Samuneva, P. Djambaski, E. Kashchieva, G. Chernev, L. Kabaivanova, E. Emanuilova, I.M. M. Salvado, M.H.V. Fernandez, A. and Wu, *J. Non-cryst. Solids*, **2008**, *354*, 733-740.
11. K.Pal, A.K. Banthia and D.K. Majumdar, *Trends Biomater. Artif. Organs*, **2006**, *20*, 59-67.
12. L.Y.Ye, Q.L.Liu, Q.G. Zhang, A.M. Zhu and G.B. Zhou, *J. Appl. Polym. Sci.*, **2007**, *105*, 3640-3648.
13. R.F.S. Lenza and W.L. Vasconcelos, *J. Non-Cryst.Solids*, **2003**, *330*, 216.
14. G. Andrade, E.F. Barbosa-Stancioli, A.A.P. Mansur, W.L. Vasconcelos and H.S. Mansur, *Biomed. Mater.*, **2006**, *1*, 221-234.
15. B.J. Holland and J.N. Hay, *Polymer*, **2001**, *42*, 6775-6783.
16. P.S. Thomas, J.P. Guerbois, G.F. Russel and B.J. Briscoe, *J. Therm. Anal. Cal.*, **2001**, *64*, 501-508.
17. P. Budrugaec, *J. Therm. Anal. Cal.*, **2008**, *92*, 291-296.
18. D.L. Gardner and I.C. McNeill, *J. Therm. Anal. Cal.*, **1969**, *1*, 389-402.

