

Dedicated to Professor Ionel Haiduc
on the occasion of his 70th anniversary

INFLUENCE OF THE ALKOXY GROUP OF THE Si-ALKOXIDES ON THE SOL-GEL PROCESS AND ON THE STRUCTURE OF THE OBTAINED GELS

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A comparative study of the hydrolysis-polycondensation of two different Si-substituted alkoxides, leading to the final hybrid inorganic-organic materials with covalent -Si-C- bonds was carried out. The methyltriethoxysilane (MTEOS) and methyltrimethoxysilane (MTMOS) were used. By gas chromatography coupled with mass spectrometry (GC-MS), nuclear magnetic resonance (²⁹Si-NMR) and infrared (IR) spectrometry, direct evidences regarding the early stages of the sol-gel process were acquired. The differences found in the first steps of hydrolysis – polycondensation reactions were connected to the effect of the ethoxy and methoxy groups bonded to the silicon atom. It was confirmed that the main differences observed in the early stages of the sol-gel process, influence the properties and the structure of the final gels, as evidenced by IR spectroscopy and scanning electron microscopy (SEM).

INTRODUCTION

Historically, the sol-gel studies were initially focused mainly to the preparation of the pure oxide materials. The possibility to incorporate the organic compounds in the inorganic matrices given by the sol-gel method opened two decades ago the gate for new materials.¹ These were called hybrid or organic-inorganic materials and show new and important properties.

Sanchez *et al.*² considered that the hybrid materials could be classified in two main classes: (I) the Class I of hybrid materials corresponds to the materials in which organic molecules, oligomers, or low organic polymers are simply embedded in inorganic matrices; (II) the Class II of hybrid materials corresponds to those materials that have a mix type of network where both organic and inorganic compounds are bonded through stronger covalent or ionic-covalent bonds.

Schmidt³ called these types of materials ORMOCERS (ORganically Modified CERamics)

or ORMOSILS (ORganically MODified SILicates) if they are based on silicon.

The first class of hybrids materials is prepared by using classical alkoxides such as tetraethoxysilane (TEOS) and different polymers, oligomers or dyes.¹ The second class of organic-inorganic materials are usually obtained from organically modified alkoxides as: R'_(4-x)Si (OR)_x (x = 1-4 and R = CH₃, C₂H₅ and R' = CH₃, C₂H₅, C₂H₄, C₆H₅). Generally, for the alkoxide pathway of the sol-gel processes it was established⁴⁻⁶ that the first steps of hydrolysis-polycondensation are very important for the future structure and properties of the final materials. Usually the identification of the molecular species formed in the early stages of the sol-gel processes was realized using Gas-Chromatography coupled with Mass Spectrometry (GC-MS)⁷⁻¹⁰ or from structural point of view by ²⁹Si-NMR spectrometry.^{6, 11-15} Beside these two classical methods used for identification of the molecular species, other methods as Gas Permeation Chromatography

(GPC)⁶ and small- and wide-angle X-ray scattering, respectively (SAXS and WAXS)¹⁶ were used with success for quantification and monitoring of species formed through the sol-gel processes.

In our previous works, both the hydrolysis-polycondensation of organically modified Si-alkoxides^{9,10,15} and the thermal stability¹⁷ of SiO₂ based inorganic-organic hybrid materials were studied.

In this paper using the GC-MS, ²⁹Si-NMR and IR spectrometry, the direct evidences were obtained for the hydrolysis-polycondensation reactions of the methyltriethoxysilane (MTEOS) and methyltrimethoxysilane (MTMOS). The differences observed in the hydrolysis-

polycondensation reactions of the two studied alkoxides were associated with the effect of different alkoxy groups, ethoxy and methoxy, respectively, present in the initial alkoxides. These differences observed in the early stages, were related with the structure and the properties of the final materials obtained after gelation, as determined by IR spectroscopy and SEM microscopy.

EXPERIMENTAL

Solutions were prepared using methyltriethoxysilane (MTEOS) and methyltrimethoxysilane (MTMOS) as Si-organic substituted alkoxides. The molar ratio and the preparation conditions are presented in Table 1.

Table 1

Chemical compositions and the reaction conditions for studied sol-gel systems

Sample	Alkoxide	Molar ratio		pH	Stirring time (min.)	Concentration*** of Cr(acac) ₃ [mol/l]	Time-to-gel (h)
		ROH	H ₂ O				
		Alkoxide	Alkoxide				
1	MTEOS	1.75*	1	3.5	20	5 x 10 ⁻³	240
2	MTMOS	1.75**	1	3.5	20	5 x 10 ⁻³	96

* R= Et; ** R= Me; ***Only in the sample used for ²⁹Si-NMR studies

For preparation of the reaction mixtures first, a solution which contains the alcohol, water and hydrochloric acid was prepared and the alkoxides were added dropwise afterwards under continuous stirring. The stirring was maintained 20 minutes after the last drop of the alkoxide was added. After the preparation of these reaction mixtures, half of the samples were stored in closed glass vials for GC-MS and IR measurements at different moments of time. Chromium acetylacetonate (Cr(acac)₃) was added to the other half of samples as a spin relaxation agent^{13,18,19} for the ²⁹Si-NMR measurements. The final concentration of Cr(acac)₃ in each sample was 5 x 10⁻³M. Once the Cr(acac)₃ addition, the solutions were immediately transferred to a closed NMR tube.

A double focus 70-Se VG Analytical Mass Spectrometer coupled with a Hewlett-Packard 5890 Gas Chromatograph was used to identify the molecular species during the sol-gel processes under the experimental conditions presented elsewhere.^{9,10}

The IR spectra of the liquid samples were recorded on a Carl Zeiss Jena Specord M-80 spectrometer. The IR measurements on liquid samples were carried out using KRS-5 standard cells with 0.001 mm length from Carl Zeiss Jena. The so-prepared solutions were injected in the cells in order to record their IR spectra. For the solid samples the measurements were done using the disc technique, by dilution of the sample in KBr. Spectral ranges from 4000 to 2800 cm⁻¹ and 1800 to 200 cm⁻¹ respectively, with a resolution of 2 cm⁻¹ were investigated.

The ²⁹Si-NMR spectra were measured, at 79.5 MHz, with a Bruker Avance DRX-400 spectrometer equipped with an inverse detection multinuclear probe. A pulse length of 4.6 μs, an acquisition time of 1s and a number of scans varying between 128 and 1024 scans were used, the line broadening being typically 4 Hz. The external lock solvent was DMSO-*d*₆

and it was introduced in a capillary, inside the NMR tubes. The ²⁹Si-NMR spectra were proton broad band decoupled, recorded at room temperature and they were electronically referenced with respect to an external tetramethylsilane standard (TMS) at 0 ppm.

The XRD patterns were performed with a PW 3020 Philips diffractometer (Cu K_α = 0.15418 nm). The Scanning Electron microscopy (SEM) study was realized using a Hitachi S4200 microscope at 25 keV.

RESULTS

The chromatograms of studied reaction mixture at the “start” and after 96 hours from the initiation of the sol-gel reactions are presented in Figure 1. As it was described in the experimental section to obtain a good homogenization of the studied reaction mixtures these were stirred for another 20 minutes after the addition of the alkoxides was finished. This moment after the stirring was stopped and was defined as the “start” point for all measurements.

The compounds separated by gas chromatography were identified by recording their mass spectra and comparing them with National Institute of Standards & Technology (NIST) library spectra and with spectra reported in our previous works.^{9,10,15,17}

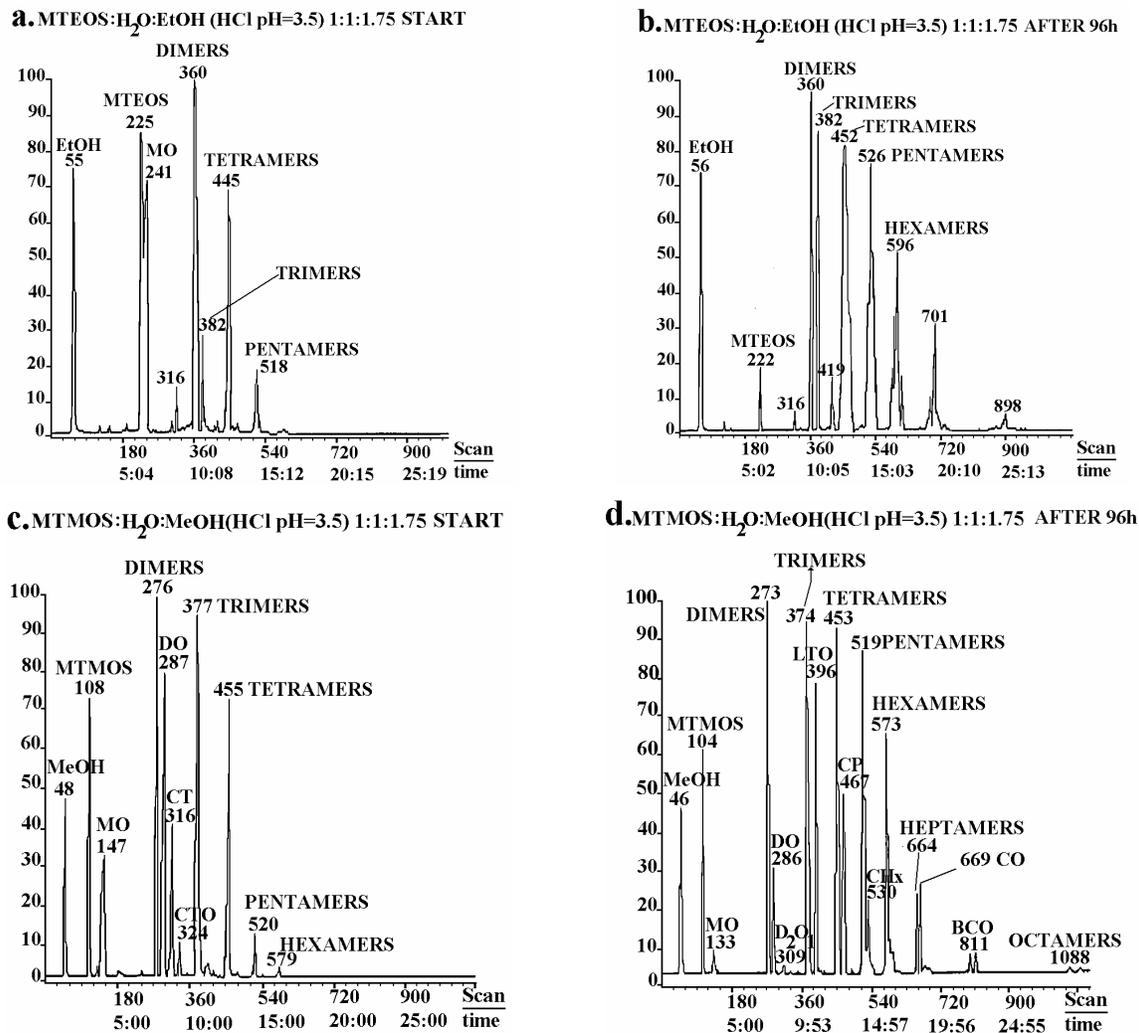


Fig. 1 – Chromatograms of the studied mixtures: a. MTEOS at “start”, b. MTEOS after 96 hours from initiation of the sol-gel reactions; c. MTMOS at “start”; and d. MTMOS after 96 hours from “start” (MO-hydroxylated monomers; DO-hydroxylated dimmers; CT-cyclic trimers; CTO-hydroxylated cyclic trimers; LTO-hydroxylated linear trimers; CP-cyclic pentamers; CHx-cyclic hexamers; CO-cyclic octamers; BCO-branch cyclic octamers).

From the recorded chromatograms, the numbers of molecular species at the “start” of reactions and after 96 hours were identified.

At the “start” of the reactions, for the solution prepared with MTMOS, as compared with that one prepared with MTEOS, a higher number of molecular species separated by gas chromatography was found. The higher number of molecular species observed by gas chromatography for the reaction mixture prepared with MTMOS could be assigned to the increasing of hydrolysis-polycondensation rate in the early stage of the process. This fact was also endorsed by the identification of molecular species with higher molecular weight in the system containing MTMOS (hexamers) as compared with the system containing MTEOS (pentamers).

After 96 hours of storage, in both cases a higher number of molecular species with higher molecular weight were identified as a result of the evolution of the hydrolysis-polycondensation process. MTMOS presents the highest reactivity, leading to formation of oligomers up to octamers, while in the case of MTEOS, molecular species with lower molecular weight, up to heptamers were noticed.

Beside these observations, in the case of MTMOS also more complex oligomers were formed as: higher number of branched cyclic and hydroxylated species such as LTO – linear hydroxylated tetramers, CP – cyclic pentamers, CHx - cyclic hexamers, CO –cyclic octamers and BCO – branched cyclic octamers. These species were not observed for the reaction mixture prepared with MTEOS.

However, the amount of monomers for the MTMOS system decrease slower than for the system prepared with MTEOS. This fact has been explained⁹ by higher number of molecular species formed initial, which are involved in a higher number of equilibriums reactions.

The ²⁹Si-NMR chemical shifts data are given in the Table 2. These data are in good agreement with the literature data.^{4,5} The data obtained at the “start” of reactions show that the rate of hydrolysis-poly-condensation is higher in the

solution containing MTMOS than in that containing MTEOS, the presence of trihydroxylated monomers and molecular species up to trimers being identified for this solution at “start”. The initial mixture starting with MTEOS, contains only monomers with lower degree of hydroxylation and dimmers.

After 96 hours from the “start”, the solution based on MTEOS contains dimers and trimers, while the solution starting with MTMOS contains dimers and tetramers.

Table 2

²⁹Si-NMR chemical shifts of reaction mixture obtained with MTEOS and MTMOS

Assigned	Chemical Shifts δ (ppm)			
	MTEOS		MTMOS	
	“Start”	96 h	“Start”	96 h
CH ₃ -Si-(OH) ₃	-	-	-38.34	-
CH ₃ -Si-(OR)(OH) ₂	-40.11	-	-	-
CH ₃ -Si-(OR) ₂ (OH)	-41.43	-	-	-
CH ₃ -Si-(OR) ₃	-42.94	-	-39.73	-
\equiv Si-O-Si-(CH ₃)(OH) ₂	-	-48.83	-47.47	-
\equiv Si-O-Si-(CH ₃)(OR)(OH)	-49.35	-49.31	-47.95	-48.01
\equiv Si-O-Si-(CH ₃)(OR) ₂	-50.77	-50.82	-	-
(\equiv Si-O) ₂ -Si-(CH ₃)(OH)	-	-57.60	-56.83	-56.91
(\equiv Si-O) ₂ -Si-(CH ₃)(OR)	-	-58.93	-	-
(\equiv Si-O) ₃ -Si-(CH ₃)	-	-	-	-65.84

From the molecular species identified by both CG-MS and ²⁹Si-NMR in the reaction mixtures containing MTMOS it may be concluded that the overall rate of the sol-gel process is enhanced for this reaction mixture comparatively with that which contains MTEOS. The higher hydrolysis rate is demonstrated by the formation of trihydroxylated monomers and dimers and the higher poly-condensation rate by the presence of a higher number of molecular species formed and the higher amount of trimers, already at the “start” of reaction.

Taking into account that in both alkoxides the same radical (-CH₃) is directly bonded to Si, the different reactivity of the studied Si-alkoxides could be connected only to the presence of different alkoxy groups. The methoxy group from MTMOS, with one carbon atom in the composition induces its higher reactivity in the sol-gel process as compared with MTEOS that contains two atoms of carbon in the alkoxy group. The obtained result is in good agreement with long time ago established behaviour of un-substituted Si-alkoxides.^{20, 21} In the later case the decreasing of the rate of the sol-gel processes with increasing

of the hydrocarbonate length of the alkoxy radical was determined.

Comparing the CG-MS results with those obtained by ²⁹Si-NMR one may notice that in the early stages of the sol-gel process GC-MS gives more detailed information being able to identify a higher number of molecular species, even when they appear in traces. The lower degree of condensation of the molecular species identified by ²⁹Si-NMR spectrometry comparatively with GC-MS is explained only by the ability of the ²⁹Si-NMR to identify the first modification around the central atom of silicon. After a number of repetitions of the sequence ...-Si-O-Si-O-Si-O-... the silicon atoms become equivalents and the signal in ²⁹Si-NMR is superposed.

The IR spectra are presented in Figures 2 and 3, respectively. These display besides the characteristic vibration bands of Si-O-Si bonds (ν_{as} Si-O-Si at 1115 and 1090 cm⁻¹, ν Si-O(H) at 975 cm⁻¹, ν_s Si-O-Si at 800 cm⁻¹, and δ Si-O-Si at 470 cm⁻¹), indicated by Bertoluzza *et al.*²² In addition, the corresponding vibrations due to the methyl groups bonded to the silicon atoms (ν_{as} CH₃ at 2980 cm⁻¹,

ν_s CH₃ at 2820 cm⁻¹, δ_s CH₃ at 1275 cm⁻¹, ν Si-C at 830 cm⁻¹ and ν_s Si-C at 670 cm⁻¹) were identified.¹⁵ Between the IR spectra of the two reaction mixtures, the highest difference was observed in the spectral range where the specific vibration of ethyl (ν_{as} CH₃ at 2980 cm⁻¹, ν_{as} CH₂ at 2860 cm⁻¹, ν_s CH₃ 2830) from ethoxy groups and for methyl (ν_{as}

CH₃ at 2980 cm⁻¹, ν_s CH₃ 2820 cm⁻¹) from methoxy group could be identified. After gelation, the absorption bands due to the presence of Si-C bonds (2980 cm⁻¹, 1275 cm⁻¹ and 830 cm⁻¹) have been identified for both precursors used. This is a direct proof that the reactions of hydrolysis-polycondensation do not affect the Si-C bond.

Fig. 2 – IR spectra of the reaction mixture obtained from MTEOS: a. at “start”, b. after 96 hours from “start”, c. after gelation.

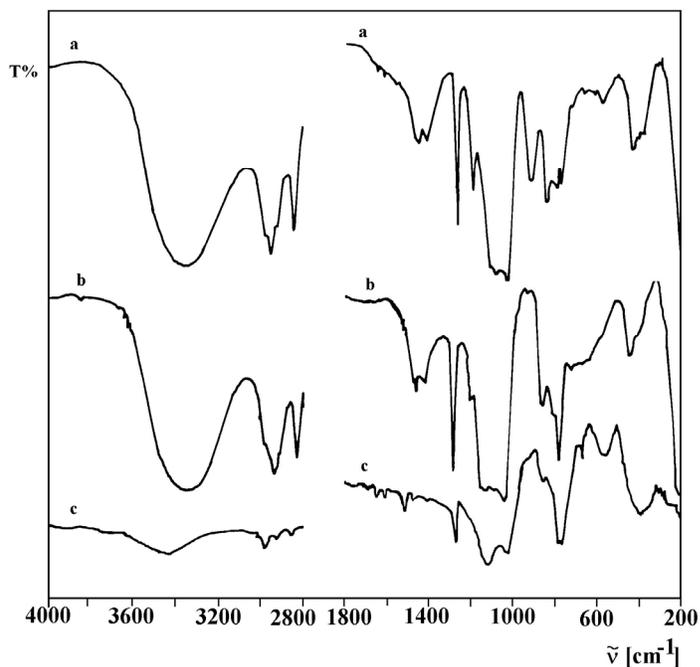
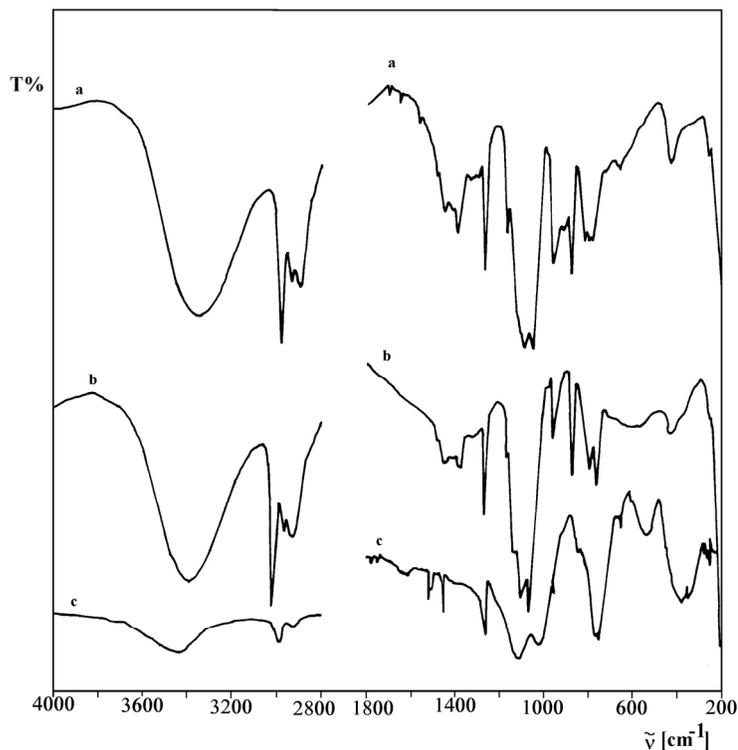


Fig. 3 – IR spectra of the reaction mixture obtained from MTMOS: a. at “start”; b. after 96 hours from “start”, c. after gelation.

As resulted from IR measurements, the characteristic vibration bands of the organic moieties present in the gels could be noticed as well as those of the silica network. However, for the gel obtained starting with MTMOS, due to the higher reactivity and consequently shorter gelation time an increased degree of disordering of the silica network was observed. This fact could be explained by a higher number of molecular species, which contributed to these vibrations. From the IR spectra of the final gels it was confirmed that during the hydrolysis-polycondensation processes, the Si-C bonds were

not affected and that the $-CH_3$ groups remain chemically bonded into the inorganic matrices.

The gelling time presented in the Table 1 is much shorter for the reaction mixture prepared with MTMOS due to its higher reactivity as compared with the solution prepared with MTEOS.

The X-ray patterns recorded for the both obtained gels are displayed in Figure 4 showing their amorphous character. As a conclusion, the IR analysis is more appropriate for structural investigation of the final gels, and the recorded differences were discussed above.

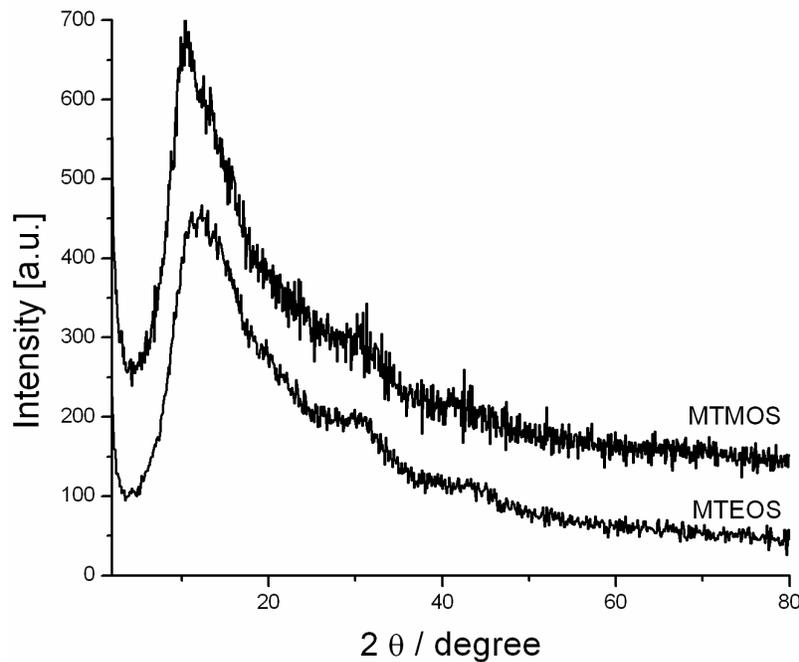


Fig. 4 – X-Ray diffraction patterns of the gels prepared using MTEOS and MTMOS.

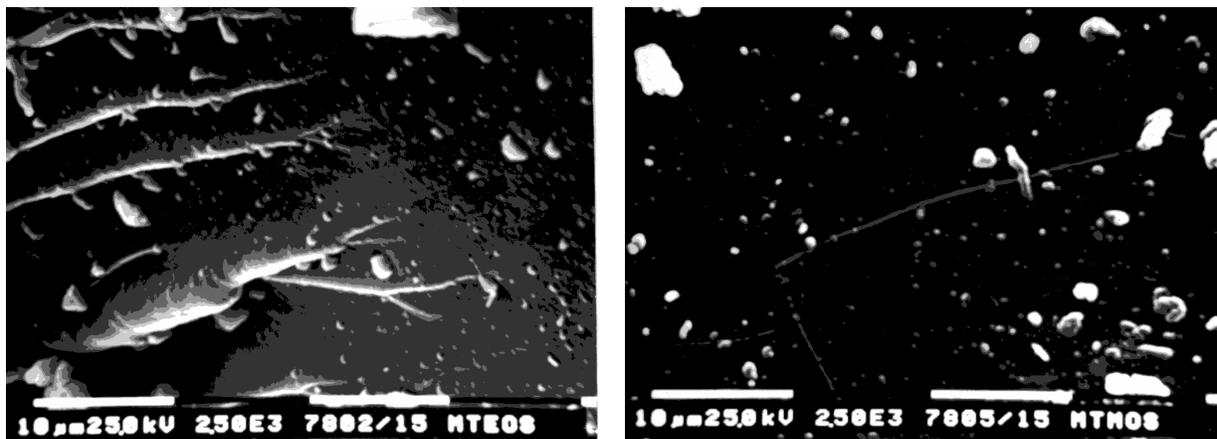


Fig. 5 – SEM images of the gels prepared with: a. MTEOS and b. MTMOS.

Some differences have been determined also in the morphology of the gels as determined by SEM. The obtained images are given in Figure 5a and 5b and have shown that a more homogeneous surface of fracture was obtained in the case of the gel prepared with MTMOS. This surface of the fracture of the gel obtained starting with MTMOS could be explained by its lower mechanical strength, due to the higher number of molecular species present in its composition. This aspect will be further investigated.

CONCLUSIONS

Sol-gel processes of the substituted Si-alkoxides (MTEOS and MTMOS), containing the same alkyl group ($-\text{CH}_3$) but different alkoxy ones ($-\text{OCH}_3$ and $-\text{OC}_2\text{H}_5$, respectively) were studied. Their reactivity depends on the alkoxy group present in the composition. The methoxy group induces a higher reactivity in the hydrolysis-polycondensation reaction.

The molecular species present in the solution at the moment of gelation influence the structure and properties of the obtained gels.

The results prove that for designing inorganic-organic materials with pre-determined structure both alkyl and alkoxy radicals present in the alkoxides' composition must be taken into consideration.

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