

Thermal decomposition of silica-methyltrimethoxysilane hybrid glasses studied by mass spectrometry

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Organically modified silicates (hybrid glasses) have attracted much attention in recent years because they are considered to be promising materials with easy tailorable new properties. The structure of hybrid glass is a silica network with incorporated organic particles or chains. A sol-gel process is a convenient method for preparing bulk glasses, as well as films and layers. The main advantage of the sol-gel technique is high homogeneity and purity of synthesised material. The sol-gel is the only method giving possibility to introduce organic molecules into the inorganic network on the molecular level. Incorporated organic molecules influence mechanical, optical and thermal properties of the silica network. Series of glasses with different amount of methyltrimethoxysilane have been prepared and characterised. Thermal decomposition of methyl modified silica hybrid glasses have been studied by DTA, FTIR and mass spectrometry.

Keywords: hybrids, decomposition, methyltrimethoxysilane, mass spectrometry.

1. Introduction

Hybrid materials are a separate group of material comprising properties of oxygen ceramics and organic polymers. Research on these materials was started by Schmidt about 15 years ago [1]. Hybrids are a comparatively new group of materials. Synthesis of hybrids is based on a sol-gel technique. The sol-gel is the only technique giving possibility to introduce organic chains into the inorganic silica skeleton. The structure of organic-inorganic materials is based mainly on a highly porous silica framework. An organic part usually fills the pores in the silica network. It is also possible to prepare hybrid materials with a mixed framework in which an organic and inorganic part is bonded together forming a three-dimensional network. The introduction of the organic material leads to elasticity of the silica network, so hybrids are usually less sensitive to cracking during drying than pure inorganic sol-gel materials [2, 3]. Hybrid materials are being applied in optics and optoelectronic [4] as a solid state electrolyte [5]

protecting coatings on glass [6] and metals [7] and as chemical sensors [8]. The application area is growing with researches on this subject. The main goal of this work was to study thermal decomposition of the silica hybrid modified by methyltrimethoxysilane (MTMS) by means of DTA equipped with the mass spectrometer. The decomposition process of the hybrids is an important factor in the case of hybrids working in higher temperature conditions.

2. Experimental

Pure grade tetraethylorthosilicate (TEOS) and methyltrimethoxysilane (MTMS) were purchased from Aldrich. Ethyl alcohol (95%) and hydrochloric acid were supplied by Polish Chemicals (POCH). Chemical compositions of the hybrids are shown in Tab. 1. TEOS and MTMS in appropriate proportion are mixed at room temperature using a magnet stirrer during 30 min, then alcohol was added under continuous stirring. Hydrochloric acid 0.05 M per 1 M of TEOS was mixed with water and dosed dropwise (exothermic reaction). The solution was mixed additionally 2 hours and then left for

Table 1. Materials used to synthesise hybrid glasses.

	TEOS	MTMS	Catalyst	Water	Solvent
Formula	$\begin{array}{c} \text{OCH}_2\text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{O} - \text{Si} - \text{OCH}_2\text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_3 \end{array}$	$\begin{array}{c} \text{OCH}_3 \\ \\ \text{CH}_3 - \text{Si} - \text{OCH}_3 \\ \\ \text{OCH}_3 \end{array}$	HCl (1 M)	H ₂ O	C ₂ H ₅ OH (95%)
Molecular weight	208.3	136.2	36.46	18.0	46.02
Content [mol]	1	0.1 to 1	0.05	2.5	2.0

gelation. Time for complete gelation (solid state body) varied from 3 to 12 hours, depending on the amount of MTMS. Gels were left for drying at room temperature during 2 weeks. FTIR absorption spectra were obtained on BIO-RAD spectrometer FTS-6000. Samples were measured using KBr technique. Thermal decomposition was studied on Q1500D DTA instrument working in air and DTA/TG TA Instruments, type SDT 2960 equipped with Balzers mass spectrometer ThermoStar GSD 300T.

3. Results and discussion

The results of standard (in air) DTA measurements of hybrids with different amounts of MTMS are shown in Fig. 1. DTA curve for the sample with 0.5 M MTMS measured in helium is shown in Fig. 2a. There are no exothermic peaks seen in Fig. 2a, as all exothermic effects are due to combustion of decomposed products and are not observed when measurements are carried out in helium. Figure 2b shows TG curve for the same

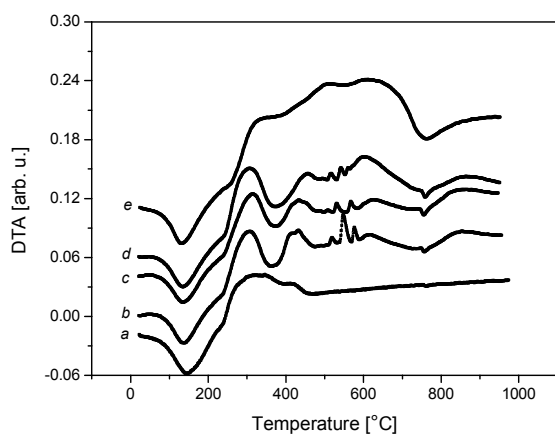


Fig. 1. DTA curve of hybrids with different amount of MTMS (for 1 M of TEOS): 0 (a), 0.2 (b), 0.5 (c), 0.7 (d), 1 (e).

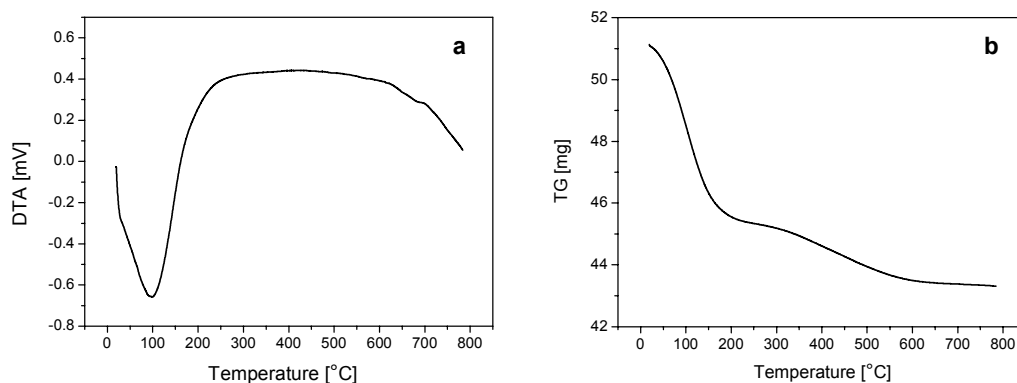


Fig. 2. Results of DTA (a) and TG (b) measurement of the sample containing 0.2 M MTMS.

sample. The main weight loss is connected with water desorption. FTIR spectra taken at characteristic decomposition temperatures (taken from DTA measured in air) are shown in Fig. 3. The IR analysis is helpful to understand structural changes during decomposition. An endothermic peak with maximum at $\sim 130^{\circ}\text{C}$, for samples measured in air and at around 110°C when the sample is measured in helium, is connected with desorption of physisorbed water. The loss of chemically bonded water (and OH groups) took place constantly at least up to 600°C , what is clearly seen from IR spectra – Fig. 3. Intensities of the bands connected with OH group vibrations 3450 , 1638 and 945 cm^{-1} are declining and eventually disappearing at 900°C – Fig. 3. The mass spectra connected with water desorption are shown in Fig. 4. The spectra have strong maximum at 113°C but the background is upraised up to 700°C and this temperature means most probably the end of water desorption. Interpretation of the exothermic

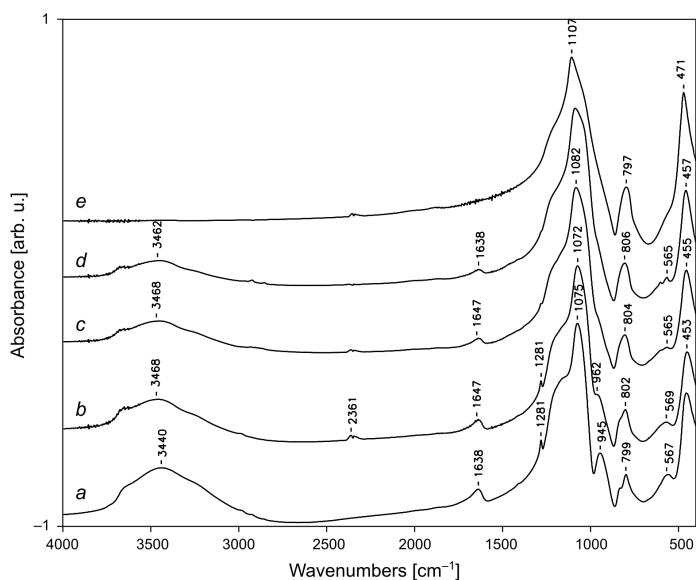


Fig. 3. MIR spectra of hybrid glasses (TEOS:MTMS = 1:0.5) as a function of thermal decomposition temperature: 120°C (a), 380°C (b), 550°C (c), 580°C (d), 900°C (e).

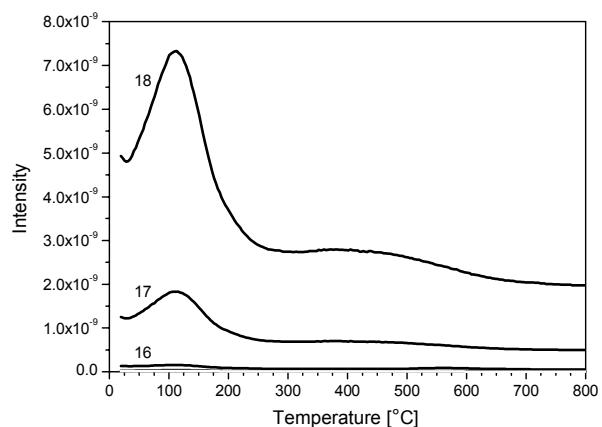


Fig. 4. Example of mass spectra as a function of temperature (masses 16, 17 and 18).

effects must be connected with the results of mass spectrometer analyses, which are summarised in Fig. 5 and Tab. 2. The desorption of water and combustion of ethane (C_2H_6) are the most intensive effects.

First exothermic effect with maximum at 145°C is due to the removal of residual ethanol and combustion of dimethyl ether (C_2H_6O) masses 29, 31 and 45, 46 [9]. At 160°C not reacted catalyst (HCl) is removed (masses 35–38). The next strong effect with maximum ~300°C – Fig. 1 is connected with the desorption of heavy

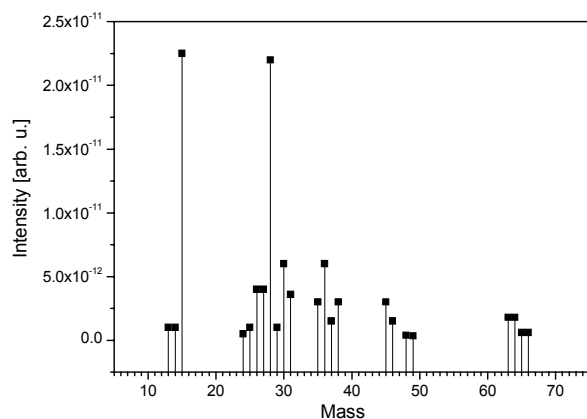


Fig. 5. Relative intensity of the masses registered by the mass spectrometer.

Table 2. Decomposition temperatures and assignment of the observed masses to the chemical compounds.

Temperature	Mass	Intensity	Assignmen
113	18	2.5×10^{-9}	H ₂ O
113	17	0.5×10^{-9}	OH
141	31	3.6×10^{-12}	C ₂ H ₅ OH
146	45	3×10^{-12}	C ₂ H ₆ O
149	46	1.5×10^{-12}	
149	29	1×10^{-12}	
155	30	6×10^{-12}	?
160	37	1.5×10^{-12}	HCl
160	38	3×10^{-12}	
163	36	6×10^{-12}	
163	35	3×10^{-12}	C ₂ H ₃ Cl
275	65	6.1×10^{-13}	
275	66	6.1×10^{-13}	
280	63	1.8×10^{-12}	C ₂ H ₃ Cl
280	64	1.8×10^{-12}	
277	48	4×10^{-13}	C ₂ H ₂
277	49	3.5×10^{-13}	
535	28	2.2×10^{-11}	C ₂ H ₄
535	26	4×10^{-12}	
535	27	4×10^{-12}	
541	24	0.5×10^{-12}	CH ₃
541	25	1×10^{-12}	
566	15	2.25×10^{-11}	CH ₃
566	13	0.1×10^{-11}	
566	14	0.1×10^{-11}	

masses: 64–65 and 48–49. Most probably these masses are due to the desorption of C_2H_5Cl formed in the sol during hydrolysis and condensation. Thermal decomposition can lead to fragmentation of C_2H_5Cl and $(C_2H_4Cl)^-$, $(C_2H_3Cl)^{2-}$, $(C_2H_2Cl)^{3-}$, CH_3Cl fragments can be produced as a result. The combustion of $(C_2H_4)^{2-}$ – masses 24–28 is observed above $400^\circ C$, decomposition temperature depending on the amount of MTMS – Fig. 1. The removal of these organic groups coincides with disappearing of the band 1281 cm^{-1} coming from Si–O–C bonds vibrations [10]. The highest temperature is needed to remove CH_3^- groups. Desorption is observed at $566^\circ C$ when the decomposition is carried out in helium or $\sim 600^\circ C$ in the case of air.

4. Conclusions

Residual ethanol and dimethyl ether are removed at $\sim 145^\circ C$. At higher temperature – $160^\circ C$ not reacted catalyst (HCl) is eliminated. A strong exothermic effect at $300^\circ C$ is connected with the removal and combustion of C_2H_5Cl . Methyl groups are the most stable and are removed at around $600^\circ C$. Physically adsorbed water is removed at $110^\circ C$, while chemically bonded water and OH^- groups are stable up to $700^\circ C$.

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