

Microstructure and optical properties of methylmethacrylate-modified silica hybrid glasses and thin films

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Silica glasses modified with organic materials offer many new, easily tailorable properties that can lead to various applications. In this work, silica–methylmethacrylate hybrid glasses have been studied. Transparent gels in the form of bulk glass and thin layers were prepared by a one-step sol-gel process. Thermal decomposition of the gels was studied by differential thermal analysis (DTA) and infrared spectroscopy (IR). Microstructure and optical properties of the glasses with different content of methacrylate were established by means of scanning electron microscopy (SEM), photoelectron spectroscopy (XPS) and UV-VIS spectroscopy.

Key words: *hybrid glasses; inorganic-organic glasses; optical properties; thin layers; microstructure*

1. Introduction

In recent years, organically modified silicates (hybrid glasses) have attracted much attention being considered as promising materials with easily tailorable new properties. The sol-gel process is a convenient method for preparation of bulk glasses as well as of films and layers. The main advantage of the sol-gel technique is a high homogeneity and purity of synthesized materials. The sol-gel is the only method enabling to introduce organic molecules into an inorganic network. Since its implementation, many hybrid glasses and ceramics have been synthesized [1–6]. Generally, hybrid materials can be classified into two classes: molecules, oligomers or polymers belonging to class I are entrapped or encapsulated within the network of base materi-

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als (usually silica network). In such a case only weak interactions between networks and entrapped material exist, based on hydrogen bonding or van der Waals forces. Hybrid materials with chemical bonds between host network and entrapped molecules belong to class II. Some of materials cannot be easily classified into one of the classes mentioned as they contain molecules bonded to the network by strong covalent or ion-covalent bonds but some molecules are simultaneously weakly bonded.

Methylmethacrylate is often used to modify the structure of silica glasses [7–10]. The bonds between an inorganic network and organic filler can be of chemical and/or physical nature and depend mainly on the composition and preparation procedures [11]. In this study, we present selected properties of hybrid materials obtained in the form of bulks and thin layers and based on the system TEOS/MMA.

2. Preparation

All hybrid glasses were prepared from pure reagents: tetraethyloorthosilicate 98% (TEOS), methylmethacrylate monomer (MMA) (Sigma-Aldrich) HCl and ethyl alcohol (Polish Chemicals). The chemicals are listed in Table 1.

Table 1. Materials used

Properties	TEOS $\text{Si}(\text{OC}_2\text{H}_5)_4$	Organic component methyl metaacrylate, MMA	Catalyst HCl	Water H_2O	Solvent $\text{C}_2\text{H}_5\text{OH}$
Molecular weight	208.3	100.1	36.46	18.0	46.02
Composition [mol]	1	0.1–1	0.05	2.5	2.0

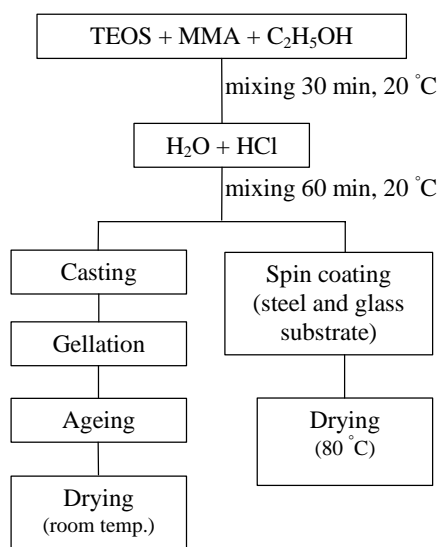


Fig. 1. Preparation scheme for silica–MMA hybrid materials

Glasses were prepared with molar ratios of TEOS to MMA ranging from 1:1 to 1:0.1. Molar ratio of TEOS:C₂H₅OH:H₂O:HCl was always 1:2:2.5:0.05. The preparation route is shown in Fig. 1. Thin layers were prepared by the spin coating technique (5000 rpm) on steel and glass substrates (microscope slides).

3. Results

3.1. Thermal stability of hybrid glasses

Thermal stability of hybrid glasses was established on the basis of DTA analysis (Q1500, Hungary). Powdered samples were heated at a rate of 10 °C/min. Selected results are shown in Fig. 2. The endothermal peak at 140 °C is due to water and remaining solvent evaporation from the porous gel. The hybrids of SiO₂/MMA glasses are stable up to 280 °C, when the decomposition begins. The first exothermal peak at 330 °C is sensitive to the MMA content in the glass (Fig. 2).

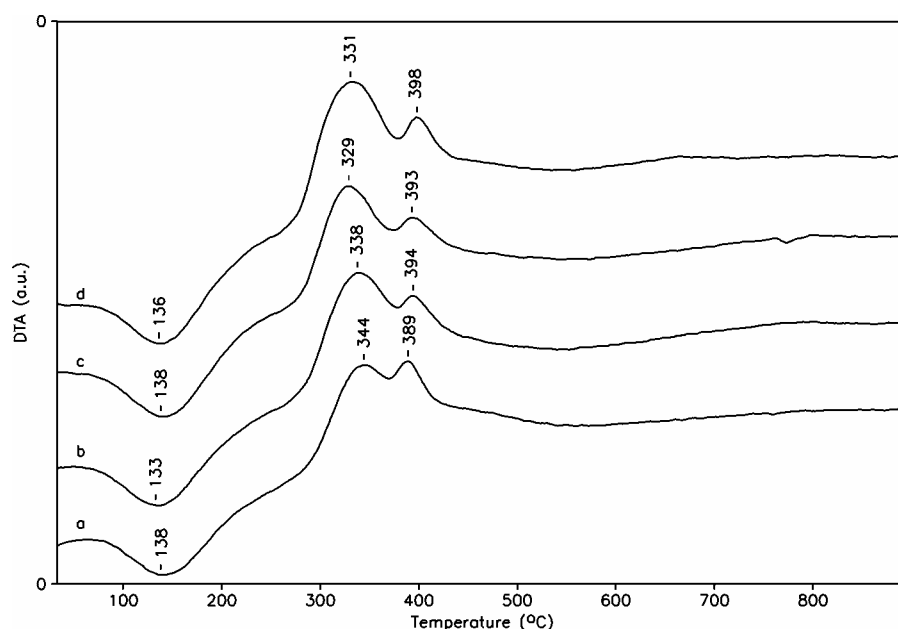


Fig. 2. DTA curves of the samples with different molar ratios of TEOS to MMA: a) 1:0.2, b) 1:0.5, c) 1:0.7, d) 1:1

This indicates that the effect is connected with the MMA decomposition. However, the exothermal peak at this position is also observed in pure silica gel prepared with a high alcohol content [12], so this exothermal effect is assumed to be due to combustion of non-hydrolyzed $-\text{OC}_2\text{H}_5$ and $-\text{OCH}_3$ groups [13,14]. Loss of $-\text{OH}$

groups chemically bonded to the silica is also possible [15]. The second exothermal peak, which appears at 400 °C, is connected with a further combustion of organic compounds (mainly $-\text{OC}_2\text{H}_5$ groups) [16].

3.2. FTIR results

To reveal structural evolution during thermal decomposition of hybrid glasses, IR spectra in a MIR region were recorded for samples thermally treated at 900, 350, 150 °C. FTIR analyses were carried out with a BIO-RAD FTS-6000 spectrometer. Absorption spectra were measured from 400 to 4000 cm^{-1} in KBr wafers with the resolution of 1 cm^{-1} . The results of the IR analysis are shown in Fig. 3. The broad band with a maximum at 3440 cm^{-1} is due to a superposition of the following stretching vibration bands [17]:

- isolated $\text{SiO}-\text{H}$ – 3750 cm^{-1} ,
- internal $\text{SiO}-\text{H}$ – 3660 cm^{-1} ,
- $\text{SiO}-\text{H}$ of surface silanols bonded to molecular water – 3540 cm^{-1} ,
- $\text{O}-\text{H}$ stretching of hydrogen bonded molecular water – 3400–3500 cm^{-1} .

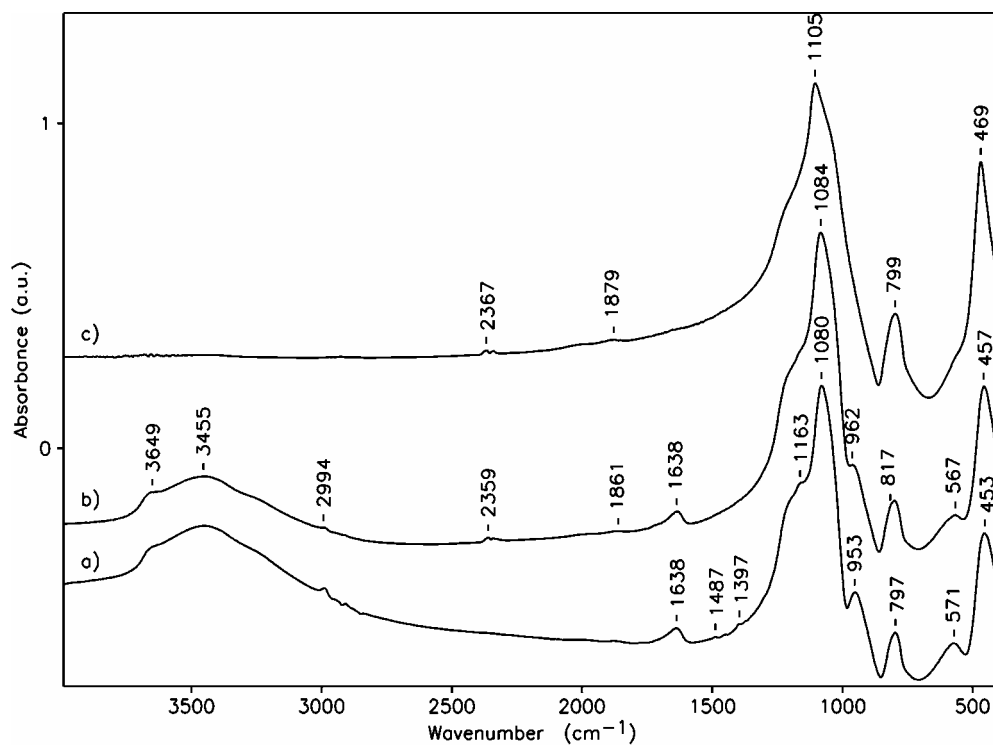


Fig. 3. MIR spectra of the samples after thermal treatment at: a) 150 °C, b) 350 °C, c) 900 °C

In addition to the vibrations corresponding to O–H bonds, the band at 1640 cm^{-1} is assigned to the deformation mode of adsorbed molecular water. All main vibration frequencies related to molecular water present in the gel are observed up to $350\text{ }^{\circ}\text{C}$ (Fig. 3c). The narrow, low-intensity bands at 2990 and $1400\text{--}1490\text{ cm}^{-1}$ correspond to the C–H stretching vibrations ($\text{H}_2\text{C}=\text{O}$, $\text{H}_3\text{C}-\text{O}-$). These bands indicate the presence of unhydrolyzed methoxy groups from methylmethacrylate. A significant decrease of their intensities at $350\text{ }^{\circ}\text{C}$ confirms that the first exothermal effect observed on DTA curve is due to combustion of $-\text{OCH}_3$ and the unreacted $-\text{OC}_2\text{H}_5$ groups. The bands at 950 and 570 cm^{-1} are attributed to silanol groups in the glass. They correspond to Si–O(H) stretching and bending vibrations, respectively. The absorption band at 950 cm^{-1} is connected with hydrogen bonding; it is present in hydrated glasses and microporous gels [17, 18]. Some contribution from the C–C stretching vibration has also been suggested [19, 20]. This band is shifted to higher frequencies as temperature increases and eventually disappears at $900\text{ }^{\circ}\text{C}$ (Fig. 3c). The most intensive band at 1080 cm^{-1} is attributed to the stretching asymmetric Si–O–Si mode, while the symmetric band of this mode is observed at 800 cm^{-1} . Bending vibrations of Si–O–Si bridges give rise to the absorption band at 460 cm^{-1} . Increase in the intensity of the bands at 800 and 460 cm^{-1} is interpreted as the formation of new Si–O–Si bridges. The band corresponding to the C=C vibration usually observed at 1700 cm^{-1} is very weak even in the gel with 1:1 TEOS to MMA molar ratio. It indicates that the C=C double bonds break during the gel formation.

3.3. Photoelectron spectroscopy

XPS spectra were recorded with a VSW spectrometer equipped with a hemispherical analyzer. Data were collected in the resolution mode FAT 22. Al K_{α} X-ray (200 W) was used as the excitation source. The spectra were adjusted to the main carbon C1s peak at the position of 284.6 eV . The results are summarized in Table 2.

Table 2. Results of XPS analysis for the sample with the composition 1:1 TEOS to MMA

Core level	Bond	Binding energy peak [eV]	Peak area [a.u.]	FWHM [eV]
C1s	C–Si	283.1	1199.4	1.35
	C–C, C–H	284.6	5206.1	1.95
	C–O	285.7	2175.8	1.95
	C=O	287.3	923.6	3.0
O1s		533.1	75224.0	2.4
Si2p		103.9	6983.4	2.4

The carbon 1s region of the samples with different contents of MMA is shown in Fig. 4. The C1s peak at 283.1 eV , visible in the spectra of the samples with high con-

tent of MMA (1:1), indicates the existence of C–Si bonds [21]. It is not observed in the samples with low content of MMA (TEOS to MMA 1:0.5 or less) (Fig. 4a). The

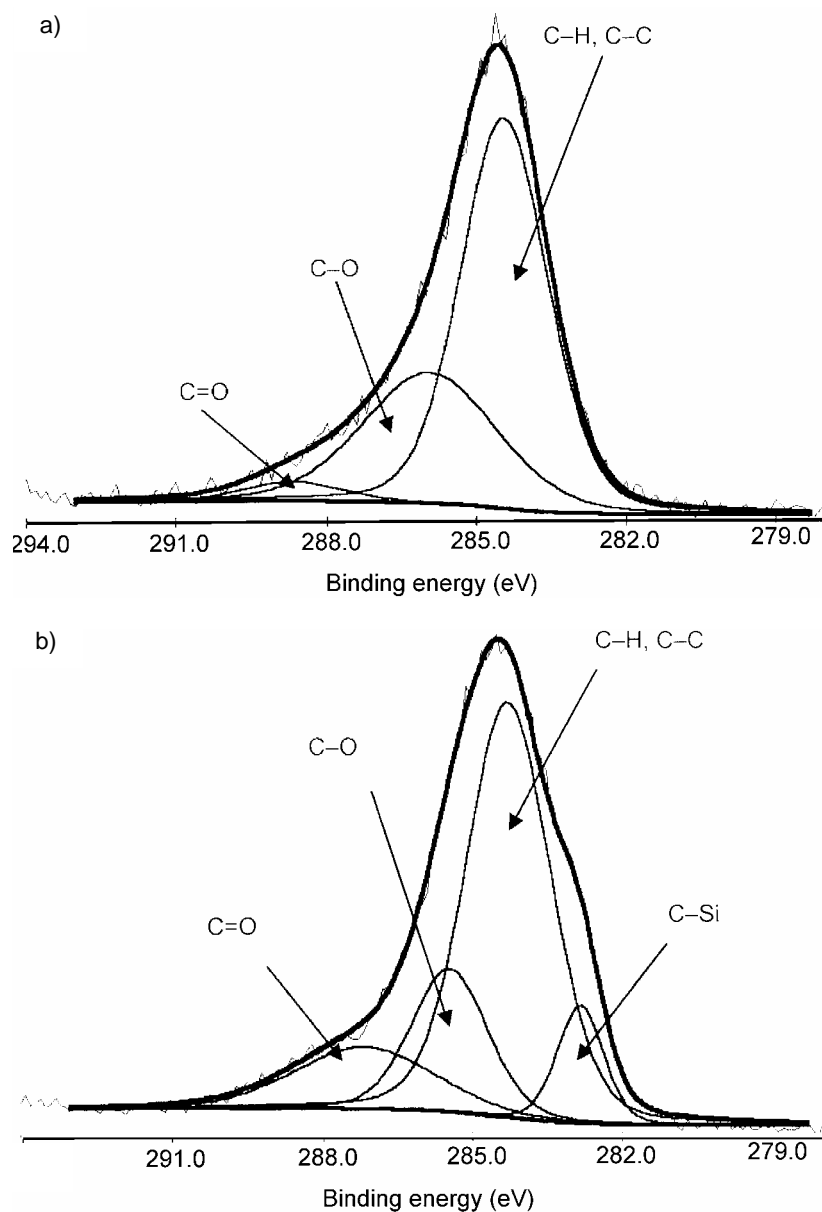


Fig. 4. XPS spectra of C1s region: a) 1:0.2 TEOS to MMA, b) 1:1 TEOS to MMA

binding energy of oxygen O 1s is relatively high (533.1 eV) and characteristic of oxygen in organic polymers having O–C–O and O–C=O bonds [21].

3.4. Spectral properties of the hybrid films

Transmittance spectra were recorded with a Perkin-Elmer Lambda 19 double-beam spectrometer in the range from 200 nm to 2.5 μm with the resolution of 1 nm.

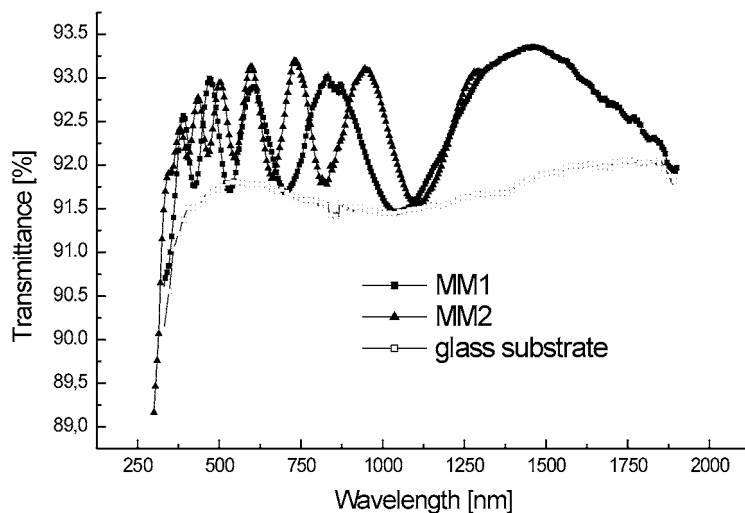


Fig. 5. Transmittance spectra of selected samples (TEOS to MMA): MM1 – 1:0.5, MM2 – 1:1

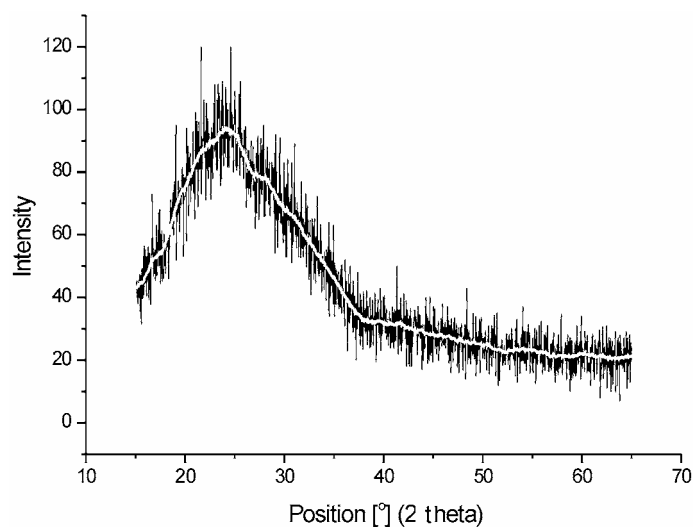


Fig. 6. X-ray low-angle (3°) diffraction analysis of the hybrid layers

Figure 5 shows the transmittance spectra of the hybrid film with the TEOS to MMA molar ratio 1:0.5 and 1:1. All films prepared on glass substrates were uniform, crack-free and transparent in the whole spectral range under investigation. X-ray low

-angle scattering measurements carried out using a Philips X Pert MPD spectrometer with the CuK_α radiation confirm that the layers are amorphous (Fig. 6). The thickness of the films measured with a Taylor-Hobson 'Tallystep' profilometer ranged from 0.7 to 1.5 μm . The thickness of the sample was a function of the MMA content and the reaction time. Thicker layers were obtained in the case of the low MMA-content samples. Increase of the MMA leads to increase in the gellation time and the increase of the viscosity is much slower. The refractive index n has been calculated from the results of the profilometer measurements and transmittance spectra from the following relationship:

$$n = \frac{1}{2d} \frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1}$$

where d is the thickness of the layer from the profilometer measurements, λ_1 , λ_2 – the wavelengths of the successive maxima in the transmittance spectra.

The refractive index calculated at 600 nm equals 1.343 for the samples with the components ratio 1:1.

3.5. Microstructure of the layers on glass and steel substrates

Microstructure of the hybrid layers has been studied with a Joel 3000 scanning electron microscope. Examples of the surface morphology are shown in Fig. 7.

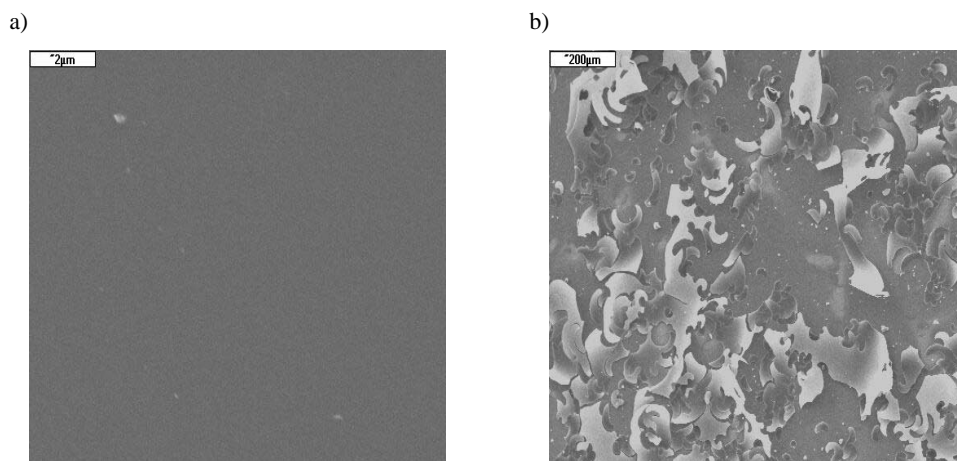


Fig. 7. SEM pictures of the hybrid layers: a) on a glass substrate, b) on a stainless steel substrate

While layers obtained on glass substrates are smooth, uniform and crack-free, layers on steel substrates are cracked with poor adherence to the substrate. The cracking was caused by differences in the thermal expansion coefficients of the hybrid layers and the steel substrates. In the case of the glass substrates, there is a high chemical compatibility between the layer and the glass and the layer is chemically bonded to

the substrate. Adherence of the hybrid layer to the stainless steel substrate is based only on physical and mechanical interactions.

4. Conclusions

The analysis of the carbon region reveals the existence of the C–Si bonds in the samples with high content of MMA. Samples having TEOS to MMA 1:1 molar ratio belong to the class II of hybrid materials; chemical bonds between the silica network and the organic filler are formed. Structures of glasses with lower contents of MMA (1:0.5 and less) are defined by the silica network with precipitates of poly-MMA in the form of short chains. Layers prepared on glass substrates are smooth, uniform and crack-free while layers on stainless steel show poor adherence to the substrates. Both, layers and bulk gels are highly transparent.

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