Silica-based *versus* silica-titania sol–gel materials – comparison of the physical properties: surface tension, gelation time, refractive index and optical transmittance

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Knowledge of the physical parameters and optical constants of sols and sol–gel materials is important in view of their possible applications. In this work, silica and silica-titania sols were examined. Gelation time, surface tension, refractive index and optical transmittance were measured. The sol–gel materials were produced from the silica precursor $Si(OC_2H_5)_4$ mixed with the titanium dioxide precursor $Ti(OC_2H_5)_4$ and 96% ethyl alcohol. It was stated that the surface tension of pure silica sols is much higher than in case of silica-titania sols. The refractive index of fresh samples is lower than of stored sols. The transmittance is highest for the fresh samples and it decreases with gelation time; however, this effect is stronger for silica-titania materials. By manipulating with the solvent content and titania addition, the required refractive index may be obtained.

Keywords: silica-titania sol–gel materials, surface tension, gelation time, refractive index, optical transmittance.

1. Introduction

Silica sol–gel materials may be produced from various silica-based precursors (non-organic, like TEOS (tetraethoxysilane, $Si(OC_2H_5)_4$), TMOS (tetramethoxysilane, $Si(OCH_3)_4$) or organic, like *e.g.*, APTES ((3-aminopropyl)triethoxysilane, $H_2N(CH_2)_3$-$Si(OC_2H_5)_3$) and suitable amount of solvent (water, alcohol, *etc.*). The proportion of used substrates influences various physical characteristics of the final material, like refractive index, porosity, density, roughness, *etc*. [1]. One may use also various additives in order to change sol–gel material parameters [2, 3]. Titanium dioxide doped materials prepared by sol–gel method are considered as, *e.g.*, promising candidates for corrosion protective coatings [4−6]. Multicomponent materials containing titanium were proved to have better adherence to the steel substrate than pure TEOS based,

however molar ratio of TEOS (tetraethoxysilane) to TEOT (tetraethyl orthotitanate, $Ti(OC_2H_5)_4$) cannot exceed 1:0.5, since higher amount of titanium results in inhomogeneity of the gels and even crystalline phase formation [4]. It is also known that titanium oxide addition results in the increase in the refractive index [7].

The main aim of our work was to examine the physical properties of the multicomponent SiO_2–TiO_2 systems (with molar ratio higher than 1:0.5) and compare them with those of pure silica sol–gel materials. Our examination showed that the main factor influencing physical properties of sol–gel materials is the amount of solvent used for materials production.

2. Materials

The sol–gel materials were produced from silica precursor TEOS and the titanium dioxide precursor TEOT (both precursors from Aldrich) in amounts depicted in the Table. All solvents and reagents were obtained from commercial sources and used without further purification. The 96% ethyl alcohol (Polish Chemicals) was added drop by drop into the mixture of precursors. Various sols were prepared: pure silica based sols without TiO_2 with various ratios $R = 5, 15, 20, 32, 40$, and 50 (R denotes solvent to precursor molar ratio) and SiO_2–TiO_2 multicomponent system. The 37% HCl (Polish Chemicals) was added as a catalyst in proportion to ensure the acid hydrolysis (pH $\approx$ 2). The mixture was stirred for 4 hours by means of a magnetic stirrer with the speed 400 rot/min at room temperature.

T a b l e. Proportions of substrates used for material production (A–H denote SiO_2–TiO_2 multicomponent materials, whereas R states for pure silica based sols).

Sample	$Si(OC_2H_5)_4$ [ml]	$Ti(OC_2H_5)_4$ [ml]	C_2H_5OH [ml]
A	5	5	7
$R = 5$	5	0	7
B	5	5	13
$R = 10$	5	0	13
C	5	5	20
$R = 15$	5	0	20
D	5	5	26
$R = 20$	5	0	26
E	5	5	39
$R = 30$	5	0	39
F	5	5	43
$R = 32$	5	0	43
G	5	5	52
$R = 40$	5	0	52
H	5	5	65
$R = 50$	5	0	65

All samples were prepared on the same day and stored at the same humidity and temperature conditions for 12 hours and then taken for examination. All measurements were also performed in the same temperature and humidity conditions ($T = 22$ °C, humidity 75%).

3. Methods

Surface tension of freshly prepared sols was examined by the capillary method [8]. The surface tension σ was calculated from the following formula:

$$\sigma = 0.5 \rho g h r \quad [\text{N/m}]$$

where ρ – liquid density [kg/m^3], g – gravitational acceleration (9.80665 m/s^2), h – average height of liquid column in capillary [m], r – capillary radius [m].

Gelation time studies were conducted on samples placed in the UV-cuvettes macro (optical length 10 mm, BRAND/Germany, diameter 10 mm×10 mm). First, initial mass of 4 ml of freshly prepared sol was measured. Then, every 24 hours (apart from weekend days) the samples mass was measured up to the moment of full gelation.

The refractive index of sols was measured by means of Abbe refractometer. For these studies, 1 ml of sol was taken and placed in the plastic test tubes. Between measurements, all samples were stored in the same temperature conditions. Day by day, 0.05 ml of material was taken out of the tube and put on the prism for refractive index measurements.

Transmittance spectra were recorded by means of the UV-VIS spectrophotometer model V-550/560/570 (Jasco). Spectra were taken every 24 hours, wavelength range 320–1600 nm (light sources: 190–350 nm deuterium lamp and 340–2500 nm halogen lamp, lamp exchange at 340 nm).

4. Experimental results

4.1. Surface tension

Surface tension together with the sol viscosity are deciding factors for the thickness of sol–gel films prepared by the dip-coating method, where the substrate is withdrawn from the liquid with known velocity [9, 10]. Taking into account the results of measurements, it was stated that proportions of substrates strictly influences the value of sols surface tension. All measurements were conducted in room temperature, where the surface tension of tested titania sol–gel materials was about 4×10^{-2} N/m. For comparison, the value of surface tension for water in room temperature is 7.2×10^{-2} N/m [8]. The values of measured surface tension are presented graphically in the diagram in Fig. 1.

The experiments showed that the material *A* made from 7.5 ml $Si(OC_2H_5)_4$, 7.5 ml $Ti(OC_2H_5)_4$, and 10.5 ml C_2H_5OH has the lowest value of surface tension. However, the material *F* made from 2.5 ml $Si(OC_2H_5)_4$, 2.5 ml $Ti(OC_2H_5)_4$, and 21.5 ml C_2H_5OH has the highest σ. The surface tension of pure silica sols is several times
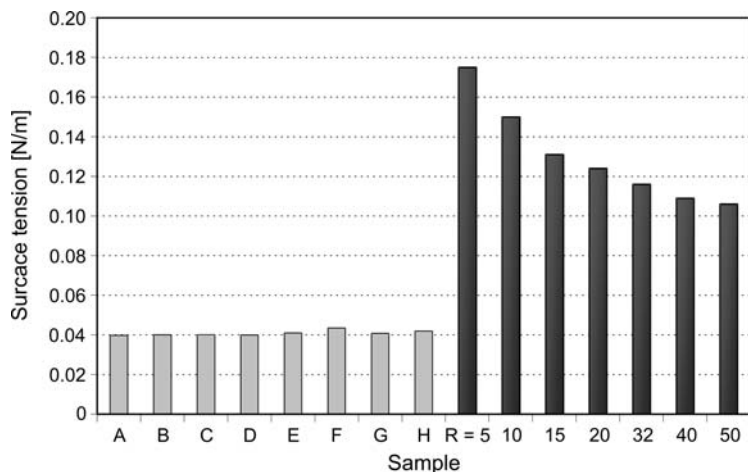
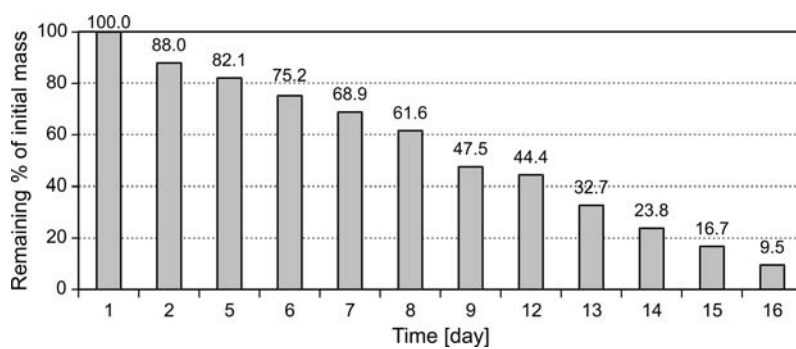Fig. 1. Graphical representation of surface tension of silica-titania and silica sols.

Fig. 2. Mass loss over time (a sample of the silica material $R = 20$, made from 5 ml $Si(OC_2H_5)_4$, and 26 ml C_2H_5OH).
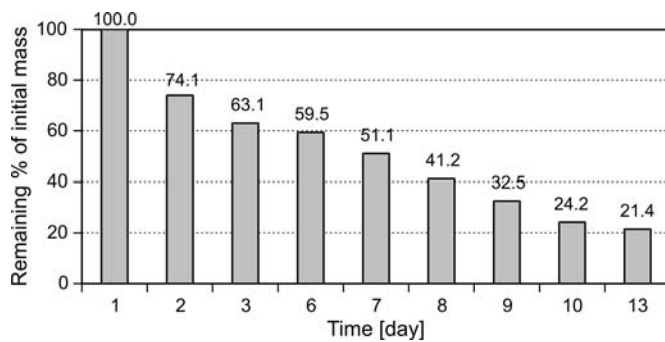
Fig. 3. Mass loss over time (a sample of the silica-titania material D, 5 ml $Si(OC_2H_5)_4$, 5 ml $Ti(OC_2H_5)_4$, and 26 ml C_2H_5OH).

higher than this of silica-titania sols. This parameter decreases with increasing R factor, which is related to alcohol content in the material.

4.2. Gelation process

Mass loss depends on gelation time, initial solvent content in a sol, and precursors properties. Presented results are mean mass values calculated on the basis of 3 series of measured samples. Gelation time for silica-based materials was 16 days and for silica-titania materials 13 days. Experimental results from the examination of silica sol prepared with $R = 20$ and silica-titania sol (sample D) made from 5 ml $Si(OC_2H_5)_4$, 5 ml $Ti(OC_2H_5)_4$, and 26 ml C_2H_5OH) are presented in Figs. 2 and 3.

For the silica-based $R = 20$ sol, mass decreased by 12% after the first day, and then by a few percent only on each further day. Between the 8th and 9th day, mass loss was 14.1%, and then in consecutive days it was 3.1%, 11.7%, 8.9%, 7.1%, and 7.2% until the gelation was completed. Mass of the remaining material is approximately 10% of the initial mass of a sol.

Silica-titania sol (sample D) lost 26% of its initial mass after the first day of gelation. Then, the mass loss was about 10% (or even less) per day. In the last day of observation approximately 21% of the material was left (see Fig. 3).

4.3. Refractive index

Refractive index is an important parameter, especially when designing the optical coatings. During gelation, the refractive index of sols increases. It also depends on the chemical composition of the sample (see Fig. 4).

The measurements of refractive index for silica-titania sols were possible in a short period only, *e.g.*, in sample C and D condensation resulted in a solid body already on the 3rd day. The refractive index of the mixture of liquids may be calculated theoretically using Lorentz–Lorentz formula [11–13]:

$$\frac{n^2 - 1}{n^2 + 2} = \phi_1\left(\frac{n_1^2 - 1}{n_1^2 + 2}\right) + \phi_2\left(\frac{n_2^2 - 1}{n_2^2 + 2}\right) + \phi_3\left(\frac{n_3^2 - 1}{n_3^2 + 2}\right)$$

Here, n is the refractive index of the mixture, n_1, n_2 and n_3 are the refractive indices of TEOS, ethyl alcohol and TEOT and ϕ_1, ϕ_2 and ϕ_3 are their volume fractions, respectively. The volume fraction ϕ may be obtained from equation $\phi_i = x_i v_i / \Sigma x_i v_i$, where x is the mole fraction and v is the molar volume of component i (where $i = 1, 2$, and 3). Mole fraction (or molar fraction) is a unit of concentration, defined to be equal to the number of moles of a component divided by the total number of moles of a mixture (*e.g.*, in a solution of 1 mol TEOS, 2 mol TEOT, and 7 mol ethyl alcohol, the mole fraction of the ethyl alcohol is 0.7). Molar volume v_i is molar mass M_i
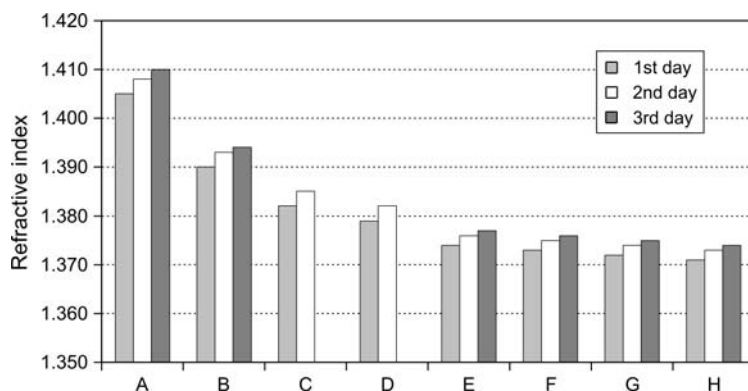
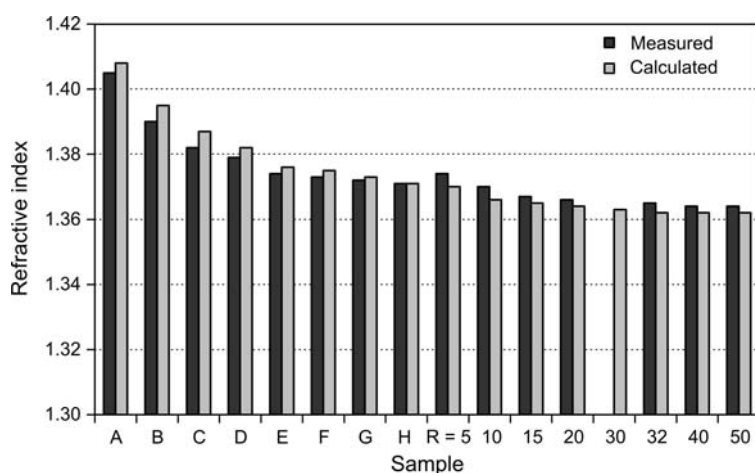Fig. 4. Refractive index of sols for various SiO_2–TiO_2 materials.

Fig. 5. Graphical representation of the comparison of the refractive indices of sols prepared with and without TiO_2 addition.

divided by density ρ_i of component *i*. The calculated values are compared with measured ones (see Fig. 5).

As one can see, it is possible to control the refractive index of samples by changing the materials composition (*e.g.*, titanium oxide or/and alcohol addition). The higher content of the ethyl alcohol in initial mixture results in the lower refractive index of sol.

4.4. Optical transmittance

For the silica-based sol–gel material with $R = 20$, the transmittance in UV and visible range varies between 90% and 100%. Lower transmittance ($\sim$60%) was observed in few last days of gelation process (see Fig. 6). In NIR spectrum the characteristic peaks are caused by the presence of water and ethyl alcohol.
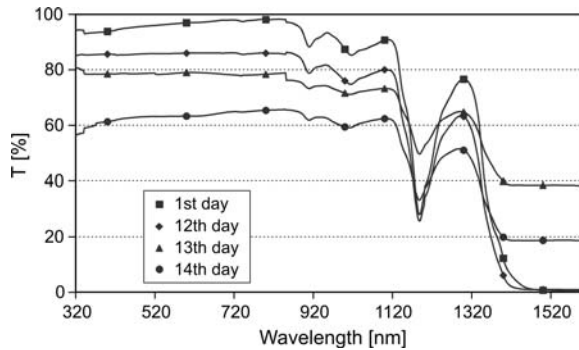
Fig. 6. Changes in transmittance with gelation time (a sample of the silica material $R = 20$, made from 5 ml Si(OC$_2$H$_5$)$_4$, and 26 ml C$_2$H$_5$OH).
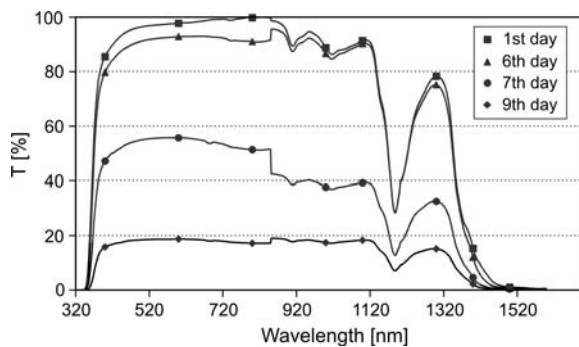

Fig. 7. Changes in transmittance with gelation time (a sample of the silica-titania material D, 5 ml Si(OC$_2$H$_5$)$_4$, 5 ml Ti(OC$_2$H$_5$)$_4$, and 26 ml C$_2$H$_5$OH).

In case of silica-titania sols, the transmittance also decreases with time (compare Fig. 7). Starting from the 9th day, the transmittance was lower than 20%. The samples were transparent. However, they cracked, causing thus scattering. In UV range, the cutoff appears at 340 nm for silica-titania sols, whereas for silica sols, the cutoff is observed for 250 nm.

The general SiO$_2$ structure can be described as a network of SiO$_4$ tetrahedra bonded at the corners. In contrast to crystalline quartz, silica glass has these units randomly oriented with respect to each other. Extrinsic contaminants such as metal ions, hydroxyl linkages or chloride reduce the transmission of silica glass at wavelengths shorter than 185 nm [14]. However, silica glass formed via the sol–gel route usually transmits poorly in the UV. Porous sol–gel silica glass supplied by a commercial vendor (Geltech of Alachua, Florida), for instance, has UV cutoffs that vary from 300 to 500 nm depending on the pore sizes [15]. Using hydrochloric acid HCl as a catalyst during the sol–gel process, UV transmission of the undoped silica sol–gel materials was found to extend down to 260 nm [16]. The addition of TiO$_2$ into the SiO$_2$ sol–gel materials shifts the cutoff into the shorter wavelength. The UV-blocking

effect of titania may be used for fabric production in textiles industry [17]. Moreover, the sol–gel materials showed photocatalytic activity by means of their antibacterial property.

The transmittance curves of silica sols and titanium oxide-doped sols in near infrared show two minima at 1180 nm and 1560 nm, characteristic of ethyl alcohol [18]. The strong absorbance at wavelengths 1180 nm and over 1560 nm appeared in spectra of all studied materials. This phenomenon is enhanced by water absorption at 1200 nm and 1470 nm. More absorbance bands of water appeared in the analyzed near infrared spectrum, because we used 96% ethyl alcohol as a solvent. Optical properties of the silica-based sol–gel materials in UV range are similar to quartz or pure silica [19]. This phenomenon is OH concentration depending [20].

5. Conclusions

Proportions of substrates used for sol preparation influence their surface tension. The surface tension of pure silica sols is much higher (more than 10×10^{-2} N/m) than surface tension of silica-titania sols ($\sim 4 \times 10^{-2}$ N/m). Moreover, the surface tension of pure silica sols varied from 0.106 N/m up to 0.175 N/m, depending on the ethyl alcohol content. The higher alcohol content in the initial mixture causes the lower surface tension of the sol. The addition of titania precursor TEOT decreases the surface tension of obtained sols.

Gelation time of pure silica sols was much longer (16 days) than silica-titania sols (11 to 13 days). The slower gelation process contributed to substantial evaporation of ethyl alcohol and after the gelation was completed, the mass of pure silica materials was 7.7–19% of the initial mixture mass. Due to the fast gelation of titanium oxide-doped materials, the observed mass loss was not so big. At the end of observation period, the mass of titanium oxide-doped materials was in the range of 21.4% to 36.2% of the initial mass. The mass loss was related to the volume of solvent and the duration of the gelation process.

The measurement of refractive indices of silica sols was possible for 10 days, while in case of silica-titania sols it was much shorter (2 or 3 days only). Generally, for both silica and silica-titania sols, refractive index decreases with increasing content of ethyl alcohol. Additions of TiO_2 caused the increase in the sols refractive index.

In visible range, the optical transmittance of the silica-based sols was very high during the whole gelation time. Acidic hydrolysis and ethyl alcohol improve the spectroscopic parameters of silica sol–gel materials [21]. As it was mentioned, in ultraviolet range spectroscopic properties of the silica sol–gel materials are similar to quartz.

In last three days (12th, 13th, and 14th day of measurement) we observed a decrease in transmittance in visible wavelengths down to 30–40% of the initial value. For all silica-titania sols, a strong decrease in transmission in the fourth day of measurement was observed. In the last day of gelation, the transmittance in visible wavelengths was around $\sim 20\%$, apart from a sample of the silica-titania material *B* (5 ml $Si(OC_2H_5)_4$,

5 ml $Ti(OC_2H_5)_4$, and 13 ml C_2H_5OH), where transmission level was 40%. The optical absorption spectra of the titania sols exhibit a step absorption edge around 320 nm [22]. We observed that silica-titania sols showed a similar cut off at 340 nm. The transparency reflects material purity and the method of manufacture. In NIR, for both silica and silica-titania sol–gel materials, absorption bands corresponding to solvents absorption (water and ethyl alcohol) were found.

The gelation process of the silica sols was a few days longer than silica-titania sols. This was caused by the fact that the silica sols cracked before the end of the observation period, although the transition from liquid sol to solid gel was less abrupt than for silica-titania sols. The sol–gel material doped with titanium oxide retained its integrity and uniform structure, allowing for cubic shape (the shape of the measurement cuvette). On the other hand, the shorter gelation time caused substantial reduction in transmittance of these materials.

Generally, we proved that it was possible to influence physical properties of silica-based sol–gel materials by the addition of titanium dioxide. The acid catalyzed silica-titania sols with different titanium content have been of interest to many groups of scientists, because physical properties of the sol–gel coating is a function of the titanium contents in silica sol. Hardness of the sol–gel coatings increases with the increasing titanium content [23].

The control of homogeneity in multicomponent systems is an important issue in sol–gel science and technology. In the specific case of TiO_2–SiO_2 sols, the very different hydrolysis rates of the precursors of the two oxides (TiO_2 and SiO_2) must be taken into account because they lead, if not appropriately controlled, to inhomogeneity of the resulting sol–gel material. Reliable and reproducible results of the measurement (*e.g.*, spectroscopic) as well as other parameters (reagent properties, temperature and humidity conditions) play important role in materials production and their applicability [24]. There are many investigations on the effect of various chemical and processing parameters, described in literature [25, 26]. Our work was focused on the measurements of the physical properties of silica-based sol–gel material doped by titanium dioxide and comparing them with those for pure silica. It was found that the amount of titanium dioxide in initial sol influences sol–gel material physical properties.

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