

Viscosity, surface tension and refractive index of tetraethylorthosilicate-based sol-gel materials depending on ethanol content

IWONA HOŁOWACZ, HALINA PODBIELSKA, JOANNA BAUER,
AGNIESZKA ULATOWSKA-JARŻA

Bio-Optics Group, Institute of Physics, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

The sol-gel-derived materials can be exploited for the number of applications, including biomaterials and measuring techniques. One of the most important applications involves production of sol-gel coatings. In this study, silica based sol-gel materials were prepared by way of acid hydrolysis with alcohol as a solvent. Tetraethylorthosilicate (TEOS) was used as a precursor. Different samples were tested; with molar ratios $R = 5, 10, 15, 20, 32$ and 50 , denoting the number of ethanol moles to the number of TEOS moles. The viscosity and surface tension of liquid hydrolyzates were measured depending on the ethanol content in sol-gel. The thickness of a coating layer was determined, as well. The refractive index was measured 10 days long, up to the point of gelation. It was demonstrated that viscosity, surface tension and refractive index are lower for higher R value (for higher alcohol content), whereas the sol-gel layers produced with higher R values are thicker than these ones produced with lower alcohol content. It is also demonstrated that R value influences the performance of fiberoptic sol-gel applicators for interstitial laser therapy.

Keywords: sol-gel coating, sol, viscosity, surface tension, refractive index.

1. Introduction

The sol-gel technique offers a low-temperature method for synthesizing materials, including fabrication of coatings. Sol-gel coatings may be used for such diverse applications as optical coatings, sensors, inorganic membranes, electrooptic and nonlinear optical films.

The sol-gel process is based on the evolution of inorganic networks through the formation of a liquid colloidal suspension (sol) and gelation of the sol to form a network in a continuous solid phase (gel). The sol-gel materials may be obtained from alkoxides $M(OR)_n$, where M stand for metal or metalloid, R (in alkoxy group) is alkyl. The alkoxide solvents may be ethanol or methanol. First, precursor is mixed

with solvent and catalyst and stirred for a few hours. The hydrolysis reaction can be catalyzed by acids or bases [1].

Various materials may be coated with liquid sol-gel product, thus changing their characteristics [2–5], preventing corrosion [6], improving biocompatibility [7] or electrical insulating properties [8]. Especially interesting are biomedical applications. Nitric oxide-releasing sol-gels are examined as antibacterial coatings for orthopaedic applications using medical-grade stainless steel [9]. To improve biocompatibility of titanium, hydroxyapatite and fluor-hydroxyapatite, sol-gel layers are deposited on titanium substrates [10]. It is possible to produce sol-gel bioactive coatings [11]. The surface of biomedical metallic implants covered by a bioactive apatite sol-gel film can create bioactivity of the implant and shorten healing time [12]. Silica gels seem also to be good materials for construction of optodes for indirect fiberoptic sensors. Their visible transparency, porosity enabling the transport of gases or liquids through the material, thermal and chemical stability, and ability to be filled with additional active phases are the key properties that gels bring to sensor applications [1, 13].

In our group, silica based sol-gel coatings are used for production of fiberoptic applicators for laser therapies [14]. Interstitial laser thermotherapy is a quite new treatment modality designed for minimal invasive destruction of pathologic tissues, whereas fiberoptics laser applicators are used to perform interstitial therapy with laser light, whereas the applicator is inserted into the pathologic lesion and curing laser light is guided through the fiber [15, 16]. We already demonstrated that sol-gel coatings may improve the characteristics of applicators. Depending on the amount of compounds used for producing sol-gels, different optical and structural properties could be achieved [17–19].

Several methods can be used to make sol-gel coatings by the sol-gel process. Generally, spin coating and dip coating are two basic techniques exploited for deposition of sol-gel layers on substrates. The thickness of sol-gel coatings is dependent on sol viscosity, surface tension and velocity of withdrawing or spinning [20]. These characteristics are influenced by material properties, like, *e.g.*, ratio R denoting the number of solvent moles to the number of precursor moles.

The purpose of our study is to measure a refractive index, viscosity and surface tension of silica sol-gel hydrolizates depending on R ratio, which corresponds to the ethanol content. These parameters are essential for construction of fiberoptics applicators for interstitial lasertherapies.

2. Experimental examination

2.1. Sol-gel preparations

The materials were obtained from silicate precursor TEOS (Fluka), solvent – ethyl alcohol 96% (POCh – Polskie Odczynniki Chemiczne S.A.), Triton X-100 (Aldrich), 36% HCl (POCh). This liquid was stirred for 5 hours by means of a magnetic stirrer with a speed of 300/min at room temperature. The corresponding amount of solvent

was used in order to obtain the required ratios R . In our study the samples were prepared with following ratios $R = 5, 10, 15, 20, 32,$ and 50 .

2.2. Refractive index measurements

The measurements of refractive indices were performed by means of an Abbe refractometer. The refractive index n of liquid is determined by using the effect of total reflection. The substance to be investigated is placed between two prisms made of highly refracting glass with refractive index N . The light passes through the illumination prism and hits the interface with the specimen under different angles (see, *e.g.*, [21]). The prepared liquid sols (each sample $20\ \mu\text{l}$) were placed on the refractometer prism for 10 days. The measurements were performed every 24 hours.

2.3. Viscosity

The viscosity of a fluid can be defined as the measure of the resistance of fluid to deformation under shear stress [22]. In this study we used Höppler viscosimeter Type BH 2. Freshly prepared sol-gel mixture was placed into the glass tube of the Höppler set. The ball (with the density equal to $2.398\ \text{g/cm}^3$) was put into the tube. The tube was closed (without air bubbles) and the falling time of the ball was measured. The measurements were performed at 22°C .

The dynamic viscosity was calculated by the following formula:

$$\eta = Kt(\rho_b - \rho_l) \quad (1)$$

where: K – constant value for the ball (cm^2/s^2), t – falling time for the ball (s), ρ_b – density of the ball (g/cm^3), ρ_l – density of the liquid (g/cm^3), η – dynamic viscosity (cP).

2.4. Surface tension

Surface tension is an effect within the surface layer of liquid that causes the layer to behave as an elastic sheet. The measurements of the surface tension were made by Wilhelmy Plate method. A thin plate is lowered to the surface of liquid and the downward force directed to the plate is measured. Surface tension is directly the force divided by the perimeter of the plate. The plate weight and the force were measured by means of torsion balance.

The surface tension σ was calculated by the following formula:

$$\sigma = \frac{F - Q}{2l} \quad (2)$$

where: F – force of tearing off, Q – plate weight, l – length of the plate.

In this study the surface tension of freshly prepared hydrolizates was measured with the use of two different plates (one was made of aluminium and the second one of copper).

2.5. Thickness of sol-gel coating

Dip coating is one of the most common ways to deposit sol-gel layers on optical fibers. If the speed and liquid viscosity are not high, the thickness may be expressed according to the following relationship derived by LANDAU and LEVICH [23]

$$h = 0.94 \frac{(\eta U)^{2/3}}{\gamma_{LV}^{1/6} (\rho g)^{1/2}} \quad (3)$$

where: η – viscosity of a liquid, U – velocity of withdrawing, ρ – density of a sol, γ_{LV} – liquid surface tension, g – gravitational constant.

The typical dip-coating involves the placement of a substrate (*e.g.*, plate, optical fiber, *etc.*) in a sol and withdrawing the object from the liquid, mostly by the use of a special device, mostly equipped with a small electric engine. Although this method is not expensive, it requires however, special equipment, careful positioning and place for a withdrawn coated object. Therefore, in our study we use a modified dip-coating method, which does not require any withdrawing engine. When depositing sol-gel layers on, *e.g.*, optical fiber, we place the fiber vertically in the container with liquid hydrolizate. The container possesses a specially designed bottom, with openings in it. The diameter of every opening can be regulated, so thus the desired outflow speed is ensured. Instead of pullout of the object, we let the sol outflow. So, no engine is necessary, we just use the gravitational force, causing the outflow through the bottom opening. So, in our case, the velocity U means the speed of the outflow.

3. Results

3.1. Refractive index

The refractive index was measured every 24 hours, at the same time each day, until the sol changed to solid. Figure 1 represents the changes of the values of refractive

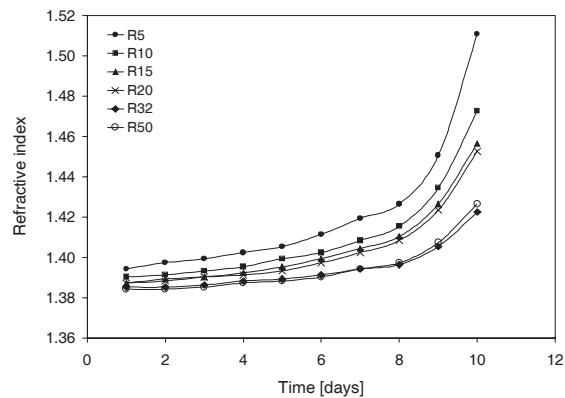


Fig. 1. Refractive index of the sol-gel hydrolizate depending on time.

T a b l e 1. Mean values of refractive indices of sol-gel hydrolyzates.

<i>R</i>	Day									
	1	2	3	4	5	6	7	8	9	10
5	1.3943	1.3973	1.3993	1.4024	1.4054	1.4114	1.4194	1.4265	1.4506	1.5108
10	1.3903	1.3913	1.3933	1.3953	1.3993	1.4024	1.4084	1.4154	1.4345	1.4727
15	1.3873	1.3893	1.3903	1.3923	1.3953	1.3993	1.4044	1.4104	1.4265	1.4566
20	1.3873	1.3883	1.3903	1.3913	1.3933	1.3973	1.4024	1.4084	1.4235	1.4526
32	1.3853	1.3853	1.3863	1.3883	1.3893	1.3913	1.3943	1.3963	1.4054	1.4225
50	1.3843	1.3843	1.3853	1.3873	1.3883	1.3903	1.3943	1.3973	1.4074	1.4265

T a b l e 2. Refractive indices of aged sol-gels (stored for 1 month).

Molar ratio <i>R</i>	15	20	32	50
Refractive index	1.5047	1.5081	1.5347	1.5693

indices n in the time. As it is demonstrated in the diagram, the refractive index is the lowest in the case of freshly prepared sol-gel hydrolyzate. With the time passing the alcohol evaporates, what causes the increase of refractive indices.

The measurements were performed on 10 samples for each R ratio. In Table 1 the mean values are shown. Generally, we observed that for lower R the refractive index is higher (the highest one for $R = 5$). Lower R denotes the lower ethanol content, so one can conclude that the amount of alcohol influences the refractive index of sol-gel hydrolyzates. With condensation time, these values became greater, what also is the result of alcohol evaporation. Finally, we have measured the refractive index of dried material (sol-gel materials stored for 1 month at room temperature). Also in this case we stated the influence of ethanol content (see Tab. 2 illustrating the results for some chosen R factors).

3.2. Viscosity and surface tension

Viscosity and surface tension were measured for freshly prepared samples, just after the end of the stirring process. The measurements were performed for 10 samples for each ratio R . The mean values are shown in Tab. 3. For better visualization of the experimental results, the data are presented in the form of diagrams. Figure 2 contains the results of viscosity measurements, whereas the surface tension values are presented in Fig. 3. As one can conclude from the measured data, both values of

T a b l e 3. Viscosity and surface tension dependent on molar ratio R .

Molar ratio R	5	10	15	20	32	50
Viscosity [mPa·s = cP]	1.926	1.778	1.759	1.704	1.699	1.634
Surface tension [N/cm]	0.0017	0.0015	0.0013	0.0012	0.0011	0.0010

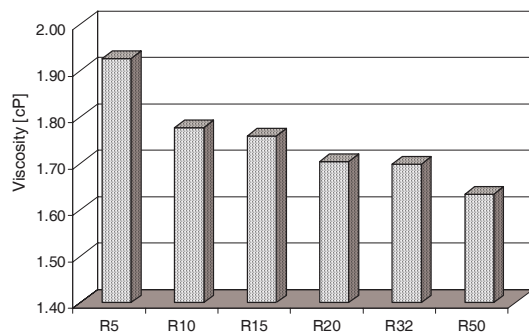


Fig. 2. Viscosity of the sols depending on ethanol content (R ratio).

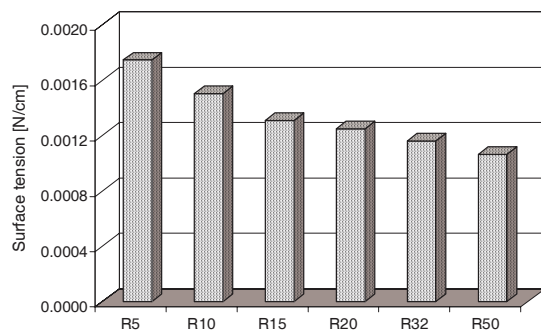


Fig. 3. Surface tension of the liquid samples depending on ethanol content (R ratio).

viscosity, as well as of surface tension, are lower for higher R value, what clearly shows that for higher alcohol content the lower viscosity and surface tension are observed.

3.3. Thickness of the sol-gel coatings

As it was already mentioned, for coatings we applied a modified “reverse” dip-coating method, where the speed of outflow was controlled by the diameter of openings in

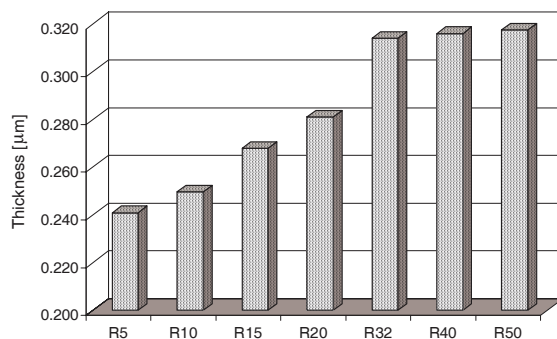


Fig. 4. Influence of ethanol content in the sol on the thickness of the coating.

T a b l e 4. Thickness of the coatings versus outflow velocity (for hole $\Phi = 0.7$ mm) and ethanol content.

Molar ratio R	5	10	15	20	32	50
U [m/s]	3.85×10^{-5}	4.18×10^{-5}	4.42×10^{-5}	4.92×10^{-5}	5.61×10^{-5}	5.88×10^{-5}
h [μm]	0.24	0.25	0.27	0.28	0.31	0.32

the bottom of the container with the sol. The outflow velocity increases with increasing ethanol content (it is higher for higher R ratio). It was already proved by STRAWBRIDGE and JAMES [24] that increasing the withdrawal speed increases the thickness, although for low viscosities the thickness variations are small [24]. The results are collected in Tab. 4 and Fig. 4.

4. Application of experimental data

The knowledge about the refractive index of a sol-gel layer, as well as about the parameters influencing the layer thickness (viscosity, surface tension, flow speed) has a practical significance, since it can be directly applied in designing fiberoptic applicators. Mentioned above parameters decide on the light distribution from an applicator tip (an exemplary image is demonstrated in Fig. 5).

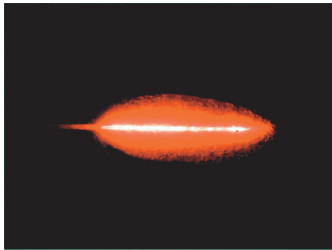
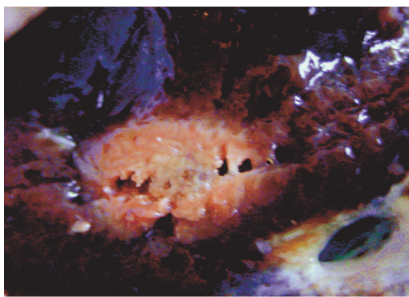
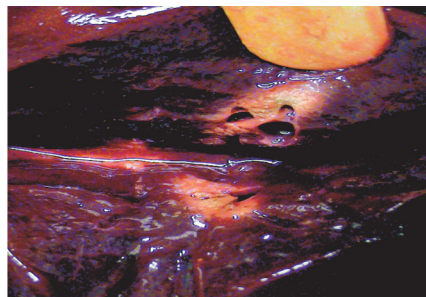


Fig. 5. Exemplary light distribution pattern from a sol-gel fiberoptic applicator.



Coagulated volumen = 5.80 cm^3
 Applicator:
 R20, 1 cm, $h = 0.28 \text{ }\mu\text{m}$,
 n of 10 days old sol = 1.4566,
 n of dried sol-gel = 1.5081



Coagulated volumen = 1.75 cm^3
 Applicator:
 R32, 1 cm, $h = 0.31 \text{ }\mu\text{m}$,
 n of 10 days old sol = 1.4225,
 n of dried sol-gel = 1.5347

Fig. 6. *In vitro* coagulation effect (Nd-YAG laser, 2.5 W, 24 ns, 30 min) with sol-gel applicators.

The applicators were also tested for coagulation of tissue *in vitro*. We demonstrated that the coagulation zone depends on the kind of sol-gel materials and it is related to the amount of ethanol. Some of these results are shown in Fig. 6, which includes the results of coagulation of porcine liver tissue *in vitro* with Nd-YAG laser and with 1 cm long sol-gel applicator.

5. Conclusions

The performed experiments demonstrated that physical parameters of sol-gel coatings may be influenced by manipulation with alcohol content as it is used as a solvent for hydrolysis. It was stated that viscosity is lower for higher R value (for higher alcohol content). Analogically we found that surface tension is lower for higher R value (for higher alcohol content). This influences the thickness of a dip-coated sol-gel layer which is higher for higher R value (for higher alcohol content). Optical parameters also show this dependence. We proved that refractive index is lower for higher R value (for higher alcohol content). These data were taken into account while designing fiberoptic sol-gel applicators for interstitial laser therapy. We demonstrated that R value influences the performance of fiberoptic sol-gel applicators for interstitial laser therapy. The greater coagulation zone is obtained for lower R value.

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