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Computer-aided microscopic examination of the structure of sol-gel glasses prepared in the form of thin films

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For the studies described here, the sol-gel matrices were prepared by way of acid hydrolysis. Thin films were procuded in the form of thin layers covering the microscopic glasses. The optical microscope was used for examination of the sol-gel glass surfaces. The sol-gel materials produced from TEOS with various molar ratios R (ratio of the number of solvent moles to the number of TEOS moles) have been examined. The microscopic images were acquired by a computer and their Sobel transforms were calculated. The analysis of the experimental data showed that the sol-gel prepared with the molar ratio equal to 32 ($R = 32$) are stable, do not crack and have smooth surface.

1. Introduction

Porous materials are defined as solids containing pores. Generally speaking, porous materials have a porosity of 0.2 – 0.95. The porosity means the fraction of pore volume to the total material volume [1]. Many porous materials have been used for many applications. They can be classified by different criteria such as pore size, pore shape, materials and production methods.

Porous materials can be produced in the sol-gel process. Sol-gel processing starts with a solution or a sol, which becomes a gel. The solution can be prepared from either inorganic salts or organic compounds, being then hydrolyzed and condensed to make a gel. One can stop at the sol stage, which refers to a dispersion of particles of colloidal dimension in a liquid, or process to the gel which means a three-dimensionally-linked network with liquid filling the pores. These pores are interconnected in the wet gel state.

The light microscope is a deceptively simple instrument, being essentially an extension of our own eyes. The range of samples characterized by the light microscopy is almost unlimited for solids and liquid crystals.

2. Preparation of materials

The chemistry of the sol-gel process comprises several steps that are well described in the literature [2], [3]. First, silicate precursor (*e.g.*, tetraethylortosilicate –

TEOS) is mixed with solvent (water or alcohol) and catalyst and stirred for a few hours. This process leads to hydrolysis of the Si–O–R bonds. The sol-gel films were prepared from the followong precursors: 5 ml TEOS (TEOS – tetraethoxysilan 98% from Aldrich) and 1.6 ml Triton X – 100 (Aldrich). The 3% HCl was added in proportion to ensure acid hydrolysis (pH = 2). The corresponding amount of solvent was used in order to obtain the required ratios R (see Tab. 1). All the precursors were mixed for 4 hours by means of a magnetic stirrer at a speed of 400/min at the room temperature. The samples were prepared in different molar ratios R (50, 32, 15 and 5).

Table 1. Sample preparation properties.

Sample No.	Molar ratio R	Type of solvent
1	5	Ethyl alcohol
2	15	Ethyl alcohol
3	15	Water
4	32	Ethyl alcohol
5	32	Water
6	50	Ethyl alcohol

The microscopic plates were first washed in water with detergent and then rinsed in doubly distilled water. Eventually, the glass plates were washed in ethyl alcohol. After alcohol evaporation they were clean and dry. Liquid hydrolyzate was spread with clean glass rod on the surface of microscopic ground glass. The thickness of the sol-gel layer was about 0.1 mm.

3. Microscopic examination

Classification of porous materials can be based on pore size. Generally, one can distinguish micropores (up to 2 nm pore diameter), mesopores (2 – 50 nm) and macropores (50 – 1000 nm) [1]. Recently, we have investigated the structure of macropores by means of light scattering measurement [4]. The nanostructure influences the morphology of the material. For many applications, the stable and homogeneous matrices with smooth surface are required, as it is in the case of sensor optodes or other optical elements [5]. Especially, the thin films used for construction of optodes should not crack and fall in to parts.

In this study, the surface of sol-gel films was examined by means of optical microscope. The microscopic image was recorded by the CCD camera and observed on a computer monitor. The Fly Video Life View frame grabber was used for image capturing. Figure 1 presents the film sample prepared with molar ratio $R = 32$, where alcohol was used as a solvent.

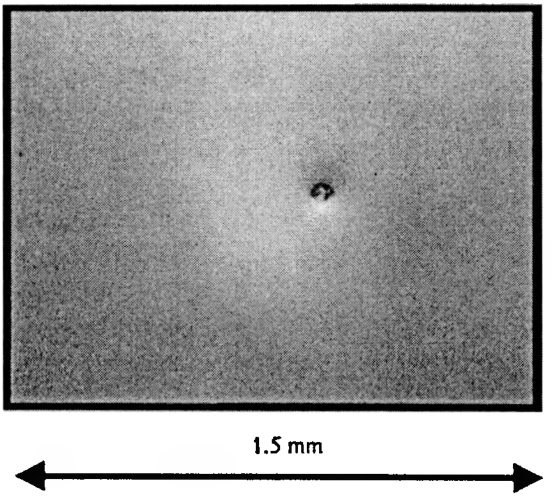

Fig. 1. Microscopic picture of the surface of the sol-gel matrix prepared with the molar ratio $R = 32$ with alcohol as a solvent. The smooth surface is observed, only small artifact is seen near the center.

4. Sobel filters for anaylsis of microscopic images

Sobel filtering is a method for enhancing the edges of an image. It produces a black and white image that has dark areas where the original image has smooth areas, and light areas where the original image has areas of rapidly varying intensity (particularly near edges). The Sobel filter replaces the center pixel of 3 by 3 neighbourhood with the sum of the absolute values of the X and Y gradients. The gradients were calculated using 3-by-3 kernels (Sobel operators), as presented in Tab. 2.

Table 2. Sobel operator.

X gradient kernel			Y gradient kernel		
−1	−2	−1	−1	0	1
0	0	0	−2	0	2
1	2	1	−1	0	1

The histogram statistics was calculated for each filtered image. The Sobel transform visualizes the edges and represent them by white pixels. More white pixels in the image denote the presence of non-homogeneities, *e.g.*, seen as scratches and cracks. Therefore, the function that calculates the content of white pixels gives immediate look at the structure. Another important factor is the mean gray value, which represents the actual mean luminescence value of pixels in the analyzed image.

5. Experimental results

All the samples given in Tab. 1 were analyzed by the procedure described above. Some of the results relating to the samples prepared with alcohol as a solvent are presented in Figs. 2 – 5.

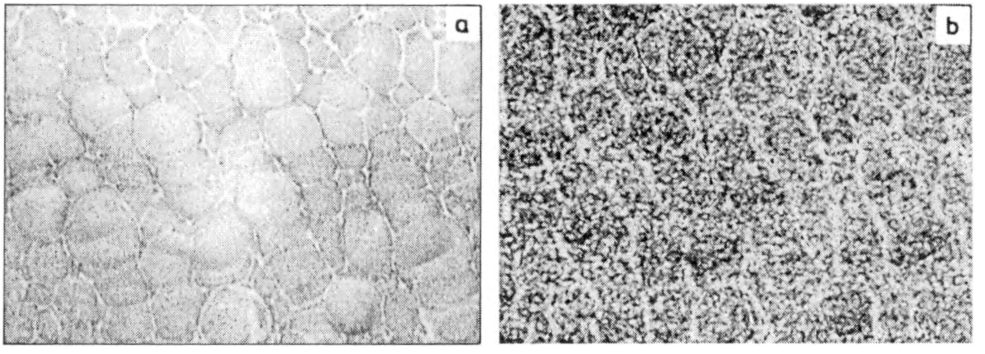

Fig. 2. Microscopic picture (a) of the surface of the sol-gel matrix prepared with the molar ratio $R = 5$ with alcohol as a solvent and its Sobel transform (b).

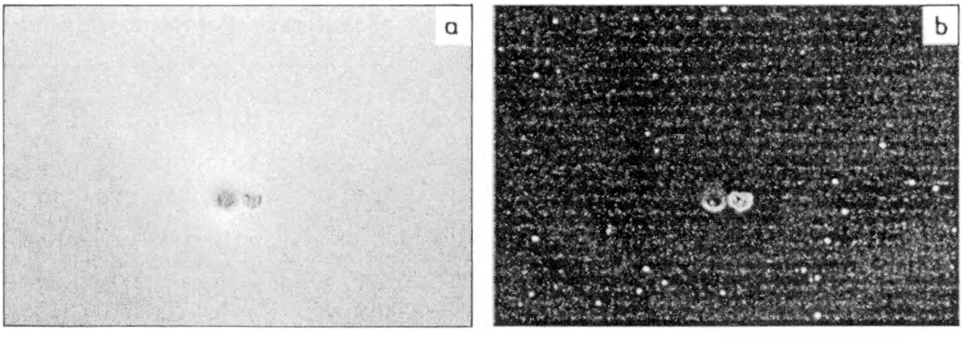

Fig. 3. Same as in Fig. 2, but for $R = 15$.

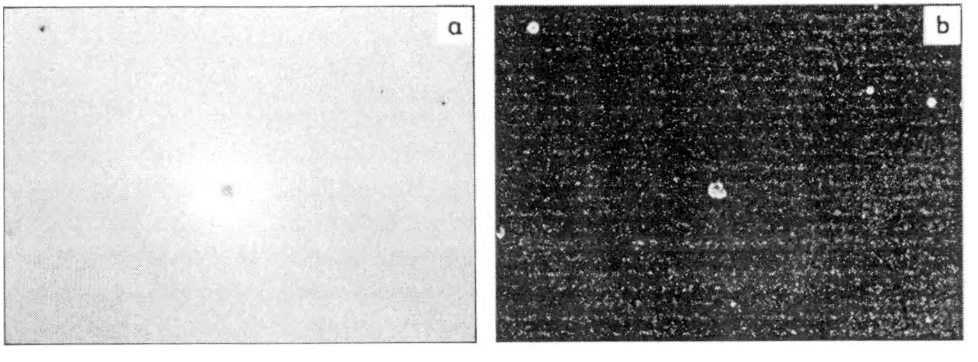

Fig. 4. Same as in Fig. 2, but for $R = 32$.

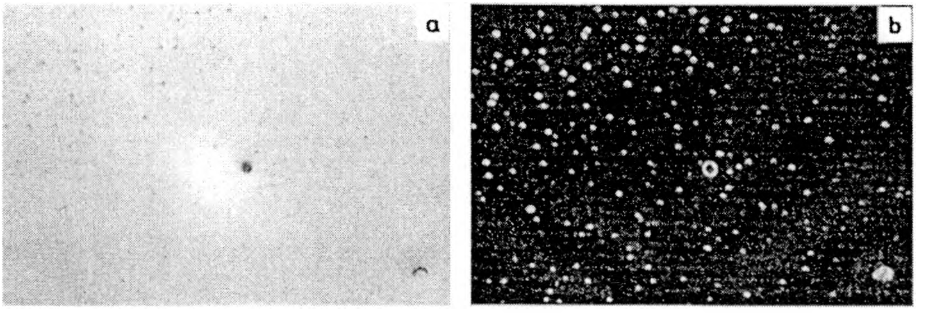

Fig. 5. Same as in Fig. 4, but for $R = 50$.

The Sobel transforms of microscopic images were calculated by means of Optimas image processing program from BioScan Optimas. The observation of images and their Sobel transforms revealed the fact that the smoothest surfaces were observed for samples prepared with molar ratio $R = 15$ and $R = 32$. The artifact near the center was especially photographed in order to demonstrate the smooth surrounding surface. The samples with molar ratio $R = 5$ show a lot of unhomogeneities compared to those made with $R = 15$, 32 and 50.

The samples that were prepared using water as a solvent have even more irregular surfaces with numerous scratches. The calculated percentage values of the full white in the images confirm that the best samples are these with molar ratio $R = 32$ prepared with alcohol (in this case the percentage of full white pixels is 0.04323 and the mean gray value is 28). The results of the analysis of image histogram statistics after Sobel filtering are presented in Tab. 3 and in Figs. 6 and 7.

Table 3. Results of histogram statistics of microscopic images after Sobel filtering.

No.	*R*	Solvent	Full white %	Mean gray value
1	5	Ethyl alcohol	0.80209	131
2	15	Water	1.31292	47
3	15	Ethyl alcohol	0.58005	31
4	32	Water	2.89289	72
5	32	Ethyl alcohol	0.04323	28
6	50	Ethyl alcohol	0.48906	32

6. Conclusions

The sol-gel thin films produced in the form of thin layers covering the microscopic glasses were examined. The surfaces were studied by means of optical microscope and computer image processing. The sol-gel materials were produced from TEOS with various molar ratios *R* with alcohol or water as solvents. The microscopic images captured by a computer were the subject of Sobel filtering. The histogram

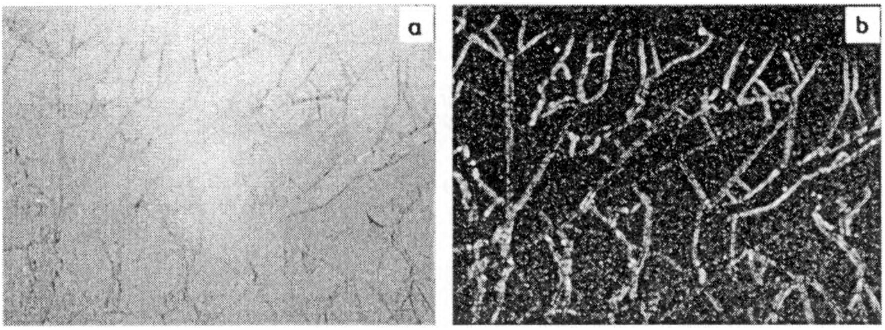

Fig. 6. Microscopic picture (a) of the surface of the sol-gel matrix prepared with the molar ratio $R = 15$ with water as a solvent and its Sobel transform (b).

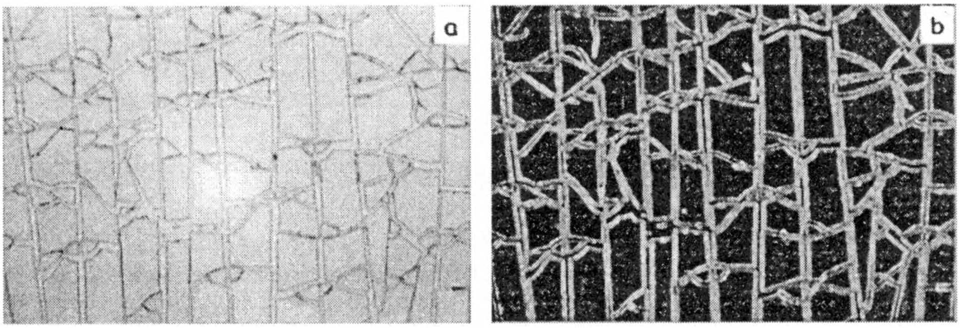

Fig. 7. Same as in Fig. 6, but for $R = 32$

analysis of Sobel images revealed the fact that the best films are those produced with alcohol as a solvent. The experimental data indicates that the sol-gel prepared with the molar ratio equal to 15, 32 or 50 are stable, do not crack and have smooth surfaces. The best results were in the case of the matrix produced with molar ratio $R = 32$. These results should be taken into account when preparing the thin film optodes for fiberoptic sensors.

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