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Effect of antibiotic insertion on photoluminescent properties of silicate porous glasses used in ophthalmologic prostheses

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The selection of silica porous glass being the most suitable material for manufacturing of the actuated scleral part of the eye prosthesis has been justified. The model explaining the photoluminescence intensity oscillations of porous glass during the effusion of the antibiotic out of the glass has been proposed. Multiple usage of the antibiotic has been found to lead to the etching effect of the porous glass and a method of minimization of the effect has been presented.

Keywords: porous glass, photoluminescence, silica gel.

1. Introduction

The aim of the present work was to test several porous silica glasses in order to check their applicability in ophthalmologic prostheses. The problem of suitable material selection is very important in prosthetic repair. The relevant materials should be biologically inert and must compensate for the lost organ as much as possible. Silicon-containing compounds are free from the deficiencies which are characteristic of organic polymers, such as the impossibility of high-temperature processing and formation of microcracks during processing [1]. They are mechanically strong and chemically stable, do not dissolve in aqueous and organic solvent, do not make a good breeding ground for microorganisms. They are not toxic and they are biologically inert. Thus, these compounds may be considered as a material suitable for prosthetic appliances [2]. The eye prosthesis usually consists of several parts. Since the parts have various purposes, they should be made of different materials. At present, the eyeball prosthesis is made of coral and the actuated scleral part is made of polymethylmethacrylate or of glass. One of the disadvantages of this type of prosthesis is the possibility of inflammatory reactions between the actuated scleral part and the eyeball prosthesis. Therefore, a search for material combinations that would not be rejected by the human organism and would prevent inflammatory reactions observed

when the scleral part is made of a solid material is extremely important. Thus, the porosity of the silica glass is especially valuable in the prevention of the above mentioned phenomena occurring between the eyeball and the actuated scleral part of the prosthesis due to its capillary diffusion.

Depending on the manufacture technology, glass may be macro- or microporous, it may contain much or little residual silica gel inside the pores [3], [4]. These characteristics of the material will affect its capillary properties and mechanical strength. Taking into account that organic substances implanted in the porous glass reveal a strongly pronounced photoluminescence, the assessment of its effusion into the surrounding medium can be performed using the luminescent techniques.

The main function of the scleral parts of the eye prosthesis, presented and studied by us, is the long-term maintenance of the biologically active substance and of its continuous effusion in the vicinity of the surface layer for interaction with the lachrymal liquid. Duration of the antiseptic retention in the porous layer should be long enough for the antiseptic to be maintained in it as long as possible without losing its basic function – prevention of the inflammatory processes under the scleral part of the prosthesis. The porous layer should not be trough (should not be percolating to the other side of the sample), otherwise the antiseptic would evaporate promptly what might result in inflammatory condition inside the eyelid due to friction on the dry porous surface. Apart from this, the totally porous prosthesis of the scleral part would undergo substantial deformation during soaring with antiseptic solution, while a thin porous layer on a thick monolithic glass does not lead to marked deformity. The scleral part of the prosthesis should be removed periodically by means of a special sucker to be soared with an antiseptic solution and to enable medical care of underlying tissues. The presence of the porous layer soaked in antiseptic allows to make this procedure relatively rare.

In order to determine the optimal thickness rate between the porous layer and the solid layer of the prosthesis, the influence of environmental humidity on the mechanical properties of the two-layer structure was examined by means of the interferometric method [5]. Luminescent studies of the diffusion rate and of the porous layer buffer properties (*i.e.*, what amount of the antiseptic can be absorbed by the porous layer and in what time it will be lost) have allowed to select the samples with the porous layer thickness of about 260 μm (it corresponds to 20-minute etching) as the most acceptable ones.

It is possible that an interaction with the antiseptic does not result in the chemical changes of the material, but in the structural changes of the pores surface. The rate of the antiseptic effusion depends first of all on the pore sizes and on porosity. Results of the effusion rate measurements obtained from the concentration change of the antiseptic effused out of the porous glass into a physiological solution – analog of the lachrymal liquid – are given in our paper [6]. Moreover, the effusion rate depends also on the level of internal surface of voids development. Results of the specific surface change for porous glass after multiple low-temperature annealing of the introduced carbon are also given in paper [6] and in our other papers [7], [8]. These results show

the increase in the specific surface area with simultaneous increase in photoluminescence intensity without changing the maximum position and the spectrum shape. It proves the increase in luminescence centers amount. The observed effects can be explained by the increase in silicon clusters amount on the inner surface of pores.

2. Experimental

Depending on the features of manufacture process, the investigated glasses were subdivided into 4 types: A, B, C and D. Glasses A and B were obtained by chemical leaching of alkali borate phase from glasses which had been submitted to phase separation at the temperature of 490 °C. Glasses B were additionally treated by KOH solution for removal of the residual fine dispersed secondary silica gel. Samples C and D were obtained similarly, but from glasses with phase separation temperature of 650 °C. Then samples D were treated by KOH. Porosity of investigated specimens was measured from the mass decrement after etching. The volume of voids was 38% for glasses A, 52% for glasses B, 41% for glasses C, and 48% for glasses D. The ability of porous glasses to maintain diffusion stability for a longer time was determined in a model environment maximally approaching real conditions. The antibiotic hentamicini sulphate was used as antiseptic. The lachrymal fluid around the porous glass was simulated by a physiological solution. The antibiotic hentamicini sulphate possesses pronounced luminescent properties. That is why the level of its effusion into the physiological solution was determined using a luminescent method.

Samples of solid glass with the thin porous layer created on their surface were investigated. The active surface of the specimens was 10×20 mm^2. An original measurement setup [9] was used for photoluminescence spectra recording. Porous glass, previously saturated with antiseptic, was placed into the quartz basin with a normal saline solution, and the antiseptics gradually evolve. The photoluminescence intensity of both the porous glass in solution and of the applied solution was measured every day. Then, the sample was placed into a fresh solution and the process was repeated until the content of the substance in the solution reached a negligible level. The criteria of "negligibility" meant approaching of the photoluminescence of the porous glass filled with antiseptic to the initial porous glass photoluminescence.

3. Results and discussion

Figure 1 shows the time dependences of photoluminescence for samples A and C. The comparison of observed dependences shows that samples A were initially soaked with antiseptic much better than the C ones. Also, samples A promptly lose a lot of the antiseptic, but the residual amounts of the antiseptics slowly and gradually are evolved. This provides a sufficient level of the antiseptic in the solution even after three weeks. samples C lost small amount of the absorbed antiseptic within the first few days of the experiment. Although certain amounts of the antiseptic remained in the porous layer,

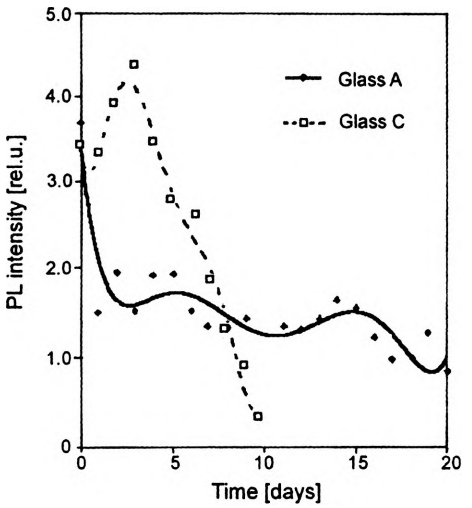
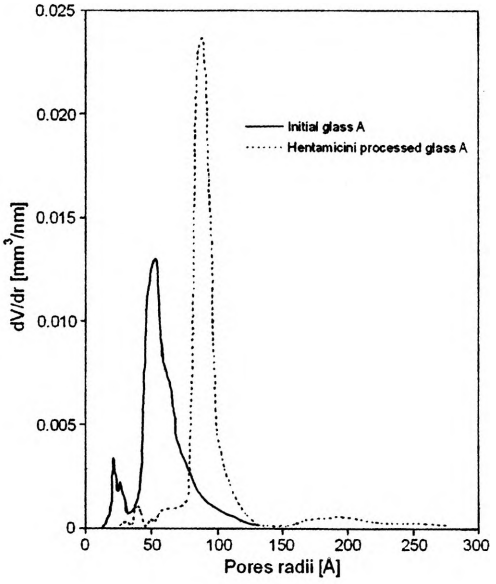


Fig. 1. Photoluminescence intensity after hentamicini sulphate processing. In Figs.1 and 3 the intensity is normalized to the intensity of photoluminescence of the initial porous glass A.

its effusion ceased after 4–5th day of changing of the physiological solution. The above results show that glasses A ensure low but permanent effusion of the antiseptic into the lachrymal liquid. This property distinguishes them from other types of the investigated glasses. It should be noted that the oscillations of the photoluminescence intensity of samples with the antiseptic are associated with the instability of the antiseptic concentration inside the pores in the process of its release into lachrymal liquid. Glasses B and D have shown a considerably smaller ability to be soaked with the antiseptic and to the subsequent effusion. The above results confirm the important role of silica gel inside pores in silica porous glasses in the process of retention and controlled evolve of the antiseptics.

In order to estimate the effect of hentamicini sulphate on porous glass, investigations of samples porosity and photoluminescence intensity change after multiple soaring with antibiotic and subsequent washing in a distillate were performed. The analysis of the pore size distribution spectrum has shown the increase in total porosity from 50 up to 58%, and also the shift of the maximum relevant to the pores size from 6 up to 10 nm. This result indicates that the hentamicini sulphate solution etches the fine pores. This leads to the increase in total porosity with simultaneous increase in medium-sized pores and the appearance of an inappreciable fraction of considerably larger pores (Fig. 2).

The analysis of the photoluminescence examinations shows the increase in its intensity in glasses after multiple hentamicini sulphate processing in all types of glasses except for D ones where the increase is inappreciable. It is explained by lowest amount of fine-disperse silica gel and larger pores for this type of glass. Comparing poroscopic results (Fig. 2) and photoluminescent studies (Fig. 1), it can be assumed that the observed process of porosity increase at multiple soaring with antibiotic is



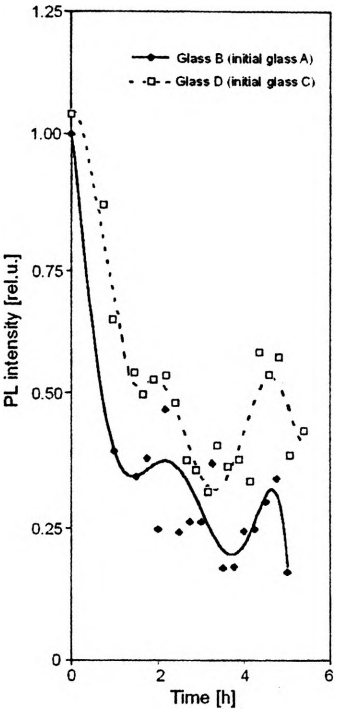


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Fig. 2. Pore-size distribution spectra for initial glass A and for hentamicini sulphate processed glass A.

Fig. 3. Dependence of photoluminescence intensity on the silica gel leaching time.

accompanied by the formation of fine-dispersed secondary silica gel. This is confirmed by the slightly acidic reaction of the hentamicini sulphate, and also by the fact that the fine-dispersed gel of secondary silica increases the internal surface of voids, which leads to the increase in luminescence intensity.

The changes in the photoluminescence intensity for porous glasses A and C in relation to the duration of KOH etching (Fig. 3) confirms this assumption. These glasses having various leaching times were obtained as a result of a special experiment. The whole of the specimens batch was immersed into an alkali solution, and then some specimens were removed from the solution every 15 minutes. This procedure was continued from 0 up to 5.5 hours.

The observed oscillations of the photoluminescence intensity can be explained by the complicated character of the interaction between the etchant molecules and the inner walls of the fine pores. The increase in KOH processing time leads initially to depleting of the etchant because of increased concentration of solved silica gel. Impeded access of a fresh alkali solution into thin capillaries leads to the formation of a supersaturated secondary silica gel solution, which settles to the bottom and this leads to the increase in photoluminescence intensity. Further increase in KOH processing time results in the inflow of fresh etchant which first of all solutes and carries away

the secondary silica gel that is situated closer to the exit from the capillaries, what leads to a diminution in the photoluminescence intensity. Supersaturation of depleted etchant with the secondary silica gel solution occurs again and the process is repeated. The longer porous glass leaching lasts, the less secondary silica gel should remain in it, what should lead to gradual decrease in a luminescence intensity.

It also explains the periodic oscillations of the photoluminescence intensity of a porous glass at the general tendency to wane in the specified time interval. The validity of similar assumptions was confirmed in [10] devoted to the formation of porous silicon from its crystalline modification as a result of composite cyclic catalytic reactions at etching in water. It is evident that similar processes take place on processing both with hentamicini sulphate, and with KOH (but in the second case they occur more intensively).

Investigations of hentamicini sulphate effusion from porous glass samples point to its role as a silica gel etchant (though it is feeble). This explains oscillations of photoluminescence intensity similar to the ones presented in Fig. 3. This is also confirmed by the prompt wane of the photoluminescence intensity for sample C in comparison with more stable results in time for samples A. The observed result is associated not only with the high content of a silica gel in sample A, but first of all with the presence of thinner capillaries. This inhibits the silica gel etching process and provides an opportunity of practical application of glasses A in the task in view. It should be noted that the requirements of the capacitive poroscopy method have compelled us to investigate the influence of hentamicini sulphate on the porosity of through-etched specimens. Therefore it is possible to assume that the dissolution of the porous layer by antibiotic will be less pronounced in real two-layer glass.

Presented effects have been confirmed by the semiempirical quantum-mechanical calculation of multiple particles system [11]. Parameters of the calculation have been selected so that to describe the structure and properties of clusters in various solids with sufficient precision [12].

4. Conclusions

The most suitable material for manufacturing of the actuated scleral part of the eye prosthesis is porous glass of type A, allowing to maintain the antibiotic level in the lachrymal liquid for about three weeks. Observed photoluminescence intensity oscillations of glass during the antibiotic effusion out of it can be explained by concentration instability of the antibiotic inside the pores during its release into the lachrymal liquid. The porous glass etching effect occurs at multiple use of hentamicini sulphate antibiotic. Nevertheless, the use of solid glass with a thin porous layer allows us to reduce the observed effect to a minimum.

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