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Effect of sol–gel synthesis conditions on the physical properties of silica hydrogels

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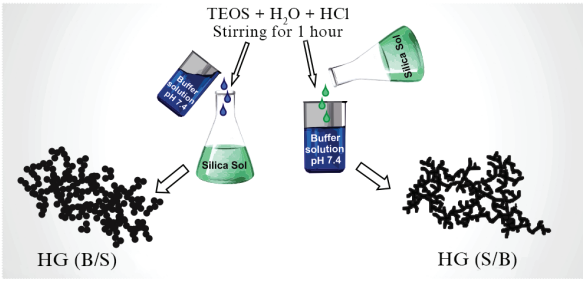
The order of mixing a silica sol and buffer solution as a neutralizing agent and the concentration of an acid catalyst for silica sol formation are of significant importance for the sol–gel synthesis of silica hydrogels with desired properties for biomedical applications. Alterations in the indicated synthesis conditions led to changes in the density and porosity of hydrogels and as well as their responses to mechanical stress (compression, tension).



Keywords: silica, hydrogel, sol–gel synthesis, order of component mixing, physical properties.

Hydrogel (HG) materials are widely used in biomedicine due to a unique combination of properties, such as biocompatibility, ability to retain water, high porosity, soft consistency, and excellent viscoelastic properties.[1,2] In cosmetology, hydrogels are often the basis of various creams, masks, and fillers for contour plastics.[3,4] Hydrogels based on natural and synthetic polymers have been intensively studied and used.[1–5] The main disadvantage of polymer hydrogels is rapid decomposition under various biological impacts (enzymes, microbes, and pH).[6–8] Silica hydrogels as an alternative to polymeric hydrogels exhibit important biological properties[9–12] and significantly higher mechanical, thermal and chemical stability.

In this work, we synthesized silica hydrogels for cosmetology medicine using a sol–gel method and studied their properties (density, porosity, mechanical properties, *etc.*). The order of addition of reaction mixture components (mixing order) is a very important synthesis condition. It is well known that the mixing order of reagents can significantly influence the products of synthesis and their yield.[13,14] For instance, Lee *et al.*[15] found that the order of addition of a catalyst in the sol–gel synthesis of calcium silicate cements affected the product yield and a Ca/Si molar ratio. Avdit *et al.*[16] showed that the sorption properties of mixed zirconium oxyhydrate and silicic acid gels depended on the mixing order of zirconium oxychloride and sodium metasilicate. Kawachi *et al.*[17] reported that different ways of addition of a silica precursor (tetraethoxysilane) in a reaction mixture, different aging conditions of the synthesized hydrogels, and different peptide catalysts led to the formation of xerogels with different porosity characteristics.

The aim of this work was to study the effect of the mixing order of components in the sol–gel synthesis of silica hydrogels on their physical properties: density, porosity, particle size, and Young's modules (modules of elasticity) under mechanical stress (compression and tension) The physical properties of the synthesized materials were measured after aging for two weeks. First, a silica sol was prepared using a silica precursor (tetraethoxysilane) and a catalyst (HCl). The hydrogels with pH ~7 were prepared by the addition of the silica sol to a phosphate buffer solution (pH 7.4) (s/b) or *vise versa* by the addition of the buffer solution to the sol (b/s). Different catalyst concentrations (0.25, 0.50, and 1.0 M) were used to study the effect of this parameter on the properties of hydrogels.

Table 1 summarizes the physical properties of the synthesized hydrogels. The mixing order and HCl concentration affected the physical parameters and the aspects of hydrogels (Figure S2 and Table S1, Online Supplementary Materials). The mixing order exerted the following effects: (1) the density of the hydrogels prepared by the addition of a buffer solution to the sol was higher; an opposite tendency was observed for the porosity; (2) a unimodal particle-size distribution was detected in the majority of hydrogels prepared by the addition of a buffer solution to silica sol, whereas a polymodal distribution was observed in the hydrogels prepared in a reverse order (Figure S1, Online Supplementary Materials). Obviously, this can be associated with the structural features of hydrogels caused by different conditions of their structuring or, more precisely, with the condensation conditions of sol particles because a pre-synthesized sol was used. When the sol (pH 1.3) was poured into the buffer solution (pH 7.4), the pH of the reaction mixture changed a little due to buffer solution properties. Getting into the buffer solution, the sol particles quickly acquired a negative surface charge hindering the aggregation of small silica particles and, hence, gel formation. Therefore, gelation occurred more slowly. This was confirmed by the measured gelation times of hydrogels formed upon different mixing orders. The gelation time of hydrogels prepared by the addition of the silica sol to the buffer solution was significantly longer than that of the hydrogels prepared in a reverse order, for instance, 1.1 and 0.2 h for HG (s/b, 1 M) and HG (b/s, 1 M), respectively. The slow gelation leads to the formation of hydrogels with less condensed and more flexible structures, which have a lower density and higher porosity than those of the hydrogels prepared by the addition of a buffer solution to the sol. The comparatively long period of gelation promotes the formation of silica particles with different

Table 1 Physical properties of silica hydrogels.

Hydrogel	Density[a]/g cm^{-3}	Porosity	Particle size/nm	Compressive Young's modulus[b]/kPa	Tensile Young's modulus[b]/kPa
HG (b/s, 0.25 M) pH 6.87	0.9700	0.92	289 PDI 0.023	14.5 ± 0.9	
HG (s/b, 0.25 M) pH 6.75	0.9363	0.95	50, 368 PDI 0.636	4.1 ± 0.3	8.2 ± 0.9
HG (b/s, 0.50 M) pH 6.75	0.9708	0.94	342 PDI 0.034	0.76 ± 0.06	0.79 ± 0.08
HG (s/b, 0.50 M) pH 6.67	0.9694	0.94	373 PDI 0.021	0.70 ± 0.06	1.2 ± 0.1
HG (b/s, 1.0 M) pH 6.79	0.9810	0.94	230 PDI 0.026	0.36 ± 0.05	0.70 ± 0.05
HG (s/b, 1.0 M) pH 6.77	0.9543	0.97	127, 775, 4804 PDI 0.834	0.15 ± 0.06	0.94 ± 0.1

[a] The uncertainty is 0.05%. [b] Mean value ± SD (n = 3).

sizes, and such hydrogels are characterized by a polymodal particle size distribution. When the buffer solution was added to the sol, the reaction mixture pH changed from acidic to neutral. In this case, the condensation rate of sol particles was significantly higher because a maximum condensation rate was achieved at pH 7.0 where both protonated and deprotonated silanols had the highest concentrations. A minimum condensation rate was found at the isoelectric point (pH ~2.0).[18] Therefore, the hydrogels with more condensed frameworks and more compact structures were formed.

Since the synthesized hydrogels can be used for the development of new soft drug formulations and cosmetic compositions (such as ointments, gels, creams, and fillers), elasticity is a very important property of hydrogel materials. The Young's modules (compressive and tensile modules) for the synthesized hydrogels were calculated from the experimental stress–strain curves (Figures 1 and 2).

Table 1 shows that the highest resistance to compression was observed in HG (b/s, 0.25 M). The opposite mixing order led to a decrease in the compressive Young's modulus of HG (s/b, 0.25 M) by a factor of 3.5. The same tendency was also observed in HG (b/s, 1.0 M) and HG (s/b, 1.0 M). These results

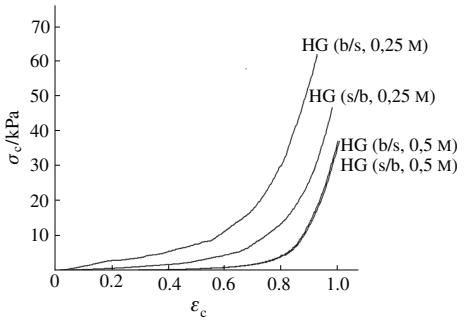


Figure 1 Compression stress–strain curves of hydrogels.

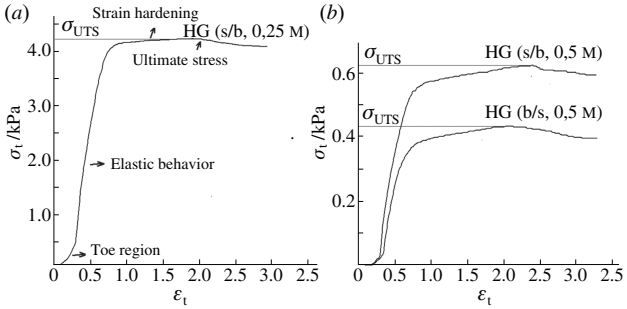


Figure 2 Tension stress–strain curves of (*a*) HG (s/b, 0.25 M) and (*b*) HG (s/b, 0.5 M) and HG (b/s, 0.5 M) (σ_{uts} is the ultimate tensile strength).

can be explained by a higher condensed structure of the hydrogels prepared by the addition of a buffer solution to the silica sol, as compared to that of the hydrogels obtained in a reverse order. The Young's modules and other studied physical properties of HG (b/s, 0.50 M) and HG (s/b, 0.50 M) did not depend on the mixing order. The compressive modulus decreased with the concentration of HCl used for the preparation of sol. This can be explained by a softer structure of the hydrogels containing larger amounts of liquid phase owing to the necessity of addition of larger amounts of a buffer solution for the neutralization of acid.

The tensile modules decreased in the following order: HG (s/b, 0.25 M) > HG (s/b, 0.50 M) > HG (s/b, 1.0 M) > HG (b/s, 0.50 M) ≈ HG (b/s, 1.0 M). Because HG (b/s, 0.25 M) is semi-solid and nonadherent, it is impossible to obtain the tensile modulus of the hydrogel. The ultimate tensile strength (σ_{UTS}), *i.e.*, the maximum stress that the sample can withstand without breaking, also decreased in the above order (Figure 2). A more flexible structure of the hydrogels obtained by the addition of sol in the buffer solution withstands higher tensile loads without breaking the materials. At the same time, the increasing amount of a liquid phase in these hydrogels makes them less stable under tension.

In summary, to optimize the conditions of the sol–gel synthesis of silica hydrogels, which are of interest for the development of drug formulations and compositions for cosmetology, we explored the effects of the mixing order of a silica sol and buffer solution and the concentration of a sol formation catalyst on the physical properties of hydrogels. The synthesis conditions can change the density and porosity of hydrogels and several times increase or decrease their response to mechanical stress (compression, tension). An increase in the catalyst (aqueous HCl) concentration led to an increase in the amount of a liquid phase in the hydrogels and their loose structures, which were less stable under mechanical stress.

This work was performed at the Institute of Solution Chemistry, Russian Academy of Sciences (state registration no. 01201260483).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.11.041.

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