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Thixotropic properties of silica-based hydrogels

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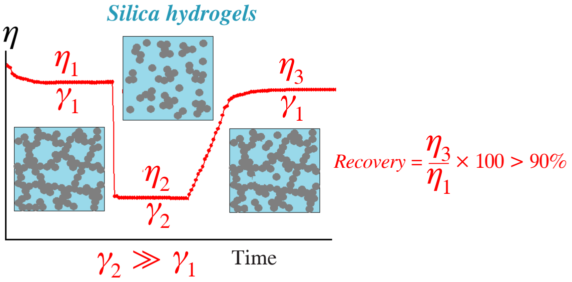
The effects of modification of a silica matrix with organic groups, the order of mixing components in a sol–gel synthesis, and the magnitude of shear loading on the thixotropic properties of silica hydrogels were studied. All synthesized hydrogels were thixotropic and restored their structure by more than 90% within 1–3 min after shear load removal. The thixotropic properties of the organically modified hydrogels and the hydrogels prepared by adding a buffer solution (pH 7.4) to a silica sol were higher due to their stronger structures.



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Thixotropic hydrogels can reduce their viscosity (liquefy) under shear stress and partially or fully recover viscosity after shear stress removal in the resting mode. This phenomenon is of great practical importance for use of hydrogels in various fields of biomedicine, such as tissue engineering and regenerative medicine,[1,2] the development of new dosage forms,[2–5] and cosmetology.[5] Due to their thixotropic properties, hydrogels can be easily and efficiently extracted from containers and applied to the skin surface or injected without spreading, thereby maintaining their shape at the injection site.

The vast majority of hydrogels already used or proposed for biomedical purposes were developed on the basis of polymers, copolymers, and their mixtures.[6–8] Many of them exhibit thixotropic properties. Studies of inorganic hydrogels for biomedical applications are very limited, although such hydrogels have a number of advantages over polymeric hydrogels (higher photostability and resistance to enzymatic and microbial attacks). Previously,[9–12] we reported the promising application of hydrogels based on colloidal silica for these purposes. Hydrogels with a fully inorganic 3D network (formed from unmodified silica particles) were investigated, and their attractive mechanical and functional properties, including thixotropic properties, were demonstrated.

This work is devoted to organically modified silica hydrogels (aminopropyl- and mercaptopropyl-modified silica). The effect of modification of a silica matrix with the above organic groups on the thixotropic behavior of the hydrogels was studied. The hydrogels were synthesized by a sol–gel method using an aqueous solution of HCl (0.250 M) as a catalyst for silica sol formation. The prepared sols were then neutralized with a phosphate buffer solution (pH 7.4) (the methodology for the synthesis of hydrogels is given in the Online Supplementary Materials). The hydrogels had pH 7, which is important for their potential biomedical applications. Previously, we found a pronounced effect of the order of mixing a silica sol and a buffer solution (the addition of a silica sol to a buffer solution or *vice versa)* on the structure and properties of unmodified silica hydrogels.[11] Therefore, the effect of this synthesis condition on the thixotropic properties of the hydrogels was also observed in this work. The hydrogels of unmodified, aminopropyl modified, and mercaptopropyl modified silica were designated as HG(b/s), HG(s/b), AHG(b/s), AHG(s/b), MHG(b/s), and MHG(s/b), respectively, where (b/s) or (s/b) refers to the order of mixing the components (a buffer solution into a silica sol or a silica sol into a buffer solution, respectively). The thixotropic properties of the hydrogels were studied by a hysteresis loop method and a three-step (three-interval) method (see Online Supplementary Materials).

The viscosity of many hydrogels decreased when mechanical forces were applied (shear-thinning effect) as a result of the breakdown of the three-dimensional hydrogel structure under mechanical loading and the organization of the resulting smaller particles in the direction of the flow.[13] However, some hydrogels partially or completely recovered their structure and viscosity after the removal of mechanical stresses. These hydrogels were thixotropic,[3,14] and their behavior was described by two curves of the dependences of apparent viscosity on increasing and decreasing shear rate, which formed a hysteresis loop. The curves plotted for the synthesized hydrogels exhibited hysteresis loops (as an example, see Figure 1); that is, the hydrogels had thixotropic properties.

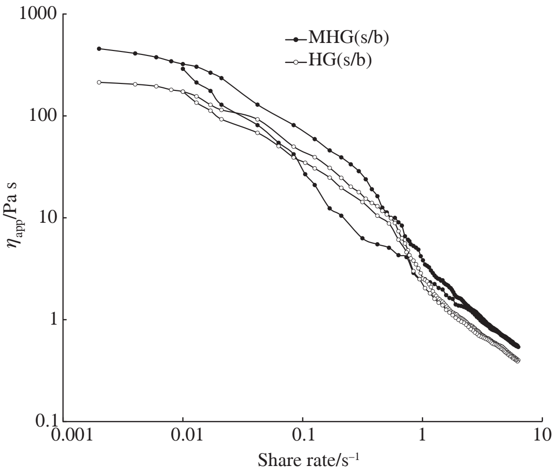

Figure 1 Hysteresis loops of HG(s/b) and AHG(s/b).

Table 1 Thixotropic properties of silica-based hydrogels.

Hydrogel	Index of thixotropy T	Degree of recovery R (%)		Time t of recovery/min	
		Shear rate $\gamma = 0.84$ s^{-1}	Shear rate $\gamma = 2.10$ s^{-1}	Shear rate $\gamma = 0.84$ s^{-1}	Shear rate $\gamma = 2.10$ s^{-1}
HG(b/s)	0.691 ± 0.018	100	99	0.8	1.7
HG(s/b)	0.595 ± 0.020	92	98	0.3	1.5
AHG(b/s)	0.706 ± 0.014	99	98	2.1	2.7
AHG(s/b)	0.605 ± 0.013	97	99	1.5	2.0
MHG(b/s)	0.711 ± 0.014	98	98	1.8	2.2
MHG(s/b)	0.620 ± 0.012	98	99	1.2	1.6

The larger the loop area, the more slowly the hydrogel restored its structure and the higher the degree of its thixotropy. The index of thixotropy (T), which is proportional to the hysteresis loop area, is a quantitative characteristic of thixotropic properties. Table 1 shows that the value of T was higher for hydrogels prepared by adding a buffer solution to a sol (b/s), and it decreased in the order MHG > AHG > HG.

The index T is a measure of energy required to break the thixotropic structure.[15,16] The more energy required to break the structure, the stronger the structure. Therefore, we can conclude that the hydrogels prepared by pouring a buffer solution into a silica sol and the mercaptopropyl-modified hydrogels had the strongest structures. The order of mixing components in the preparation of purely inorganic silica hydrogels affected the kinetics of gel formation, and the hydrogels with stronger structures were obtained when a buffer solution was added to a sol.[11] Obviously, the same effect was observed in organically modified hydrogels.

More pronounced thixotropic properties of organically modified hydrogels compared to unmodified silica hydrogels can be related to the interactions of organic groups with surface silanol groups,[17,18] which contributed to the strengthening of the three-dimensional structure of hydrogels. The highest level of thixotropy for MHG can be attributed to the ability of mercapto groups to be readily oxidized in air with the formation of disulfide bridges,[18] which further strengthened the hydrogel structure. Thus, the strength of a hydrogel structure can be increased by enhancing interactions between the silica particles forming the hydrogel framework. In addition, the hydrophobic fragments of the organic groups can contribute to the structuring of water in the hydrogels[19,20] and thus strengthen hydrogels due to hydrophobic hydration. Note that the observed effect of modification of a silica matrix of the hydrogels was somewhat different from that described previously,[21] where silica hydrogels were synthesized using other concentrations of an ash formation catalyst.

To find out how long the hydrogels recover their viscosity and to quantify the degree of their recovery, we studied the thixotropic properties of the hydrogels using a three-step method. During the testing, the apparent viscosity dependences of the hydrogel samples exposed for certain time intervals to a low shear rate ($\gamma = 0.01$ s^{-1}), then to elevated shear rates ($\gamma = 0.85$ or 2.10 s^{-1}), and again to a low shear rate ($\gamma = 0.01$ s^{-1}) were obtained. The elevated shear rates correspond to these parameters in some physiological systems[22,23] and technological processes.[24] As an example, Figure 2 shows these dependences for the hydrogels obtained by adding a buffer solution to a silica sol. Table 1 summarizes the degrees (R) and times (t) of viscosity recovery of the hydrogels after shear loading. As can be seen, the hydrogels recovered viscosity by more than 90%. This means that the three-dimensional structure of the hydrogels destroyed by the increased shear rate was formed again after the removal of shear load. As an example, Figure 2 shows the results of the three-step test for the hydrogels obtained by adding a buffer solution to a silica sol. The curves for the other samples were similar to those shown in Figure 2.

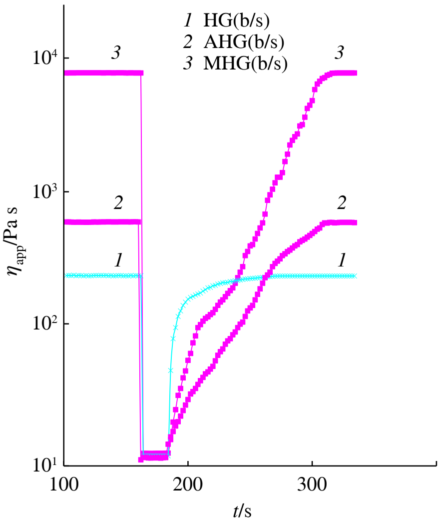

Figure 2 Three-step thixotropic test results for hydrogels prepared by adding a buffer solution to silica sols.

The recovery of the hydrogels after removal of shear load occurred within a short period of time, from 0.3 to 2.7 min. However, the unmodified silica hydrogels required shorter recovery times compared to the organically modified hydrogels (see Table 1). When shear load was applied, the interactions between silica particles and their aggregates in the three-dimensional frameworks of the hydrogels were disrupted. After the load removal, the recovery of interactions between the particles and aggregates involving longer more flexible organic groups required more time compared to that for the unmodified particles. Thus, the organic groups somewhat inhibited the structural recovery of the hydrogels. The results also showed a slower recovery of the hydrogels prepared by adding a buffer solution to a silica sol; this can be due to their stronger and more organized structures.[11] The recovery time increased slightly with the shear rate applied in the second step of the test.

In general, the experimental results showed that silica-based hydrogels are attractive for the development of materials with thixotropic properties. The influences of modification of a silica matrix with organic groups, the order of mixing components in the sol–gel synthesis, and the shear rate on the thixotropic properties of the hydrogels can serve as tools for controlling their thixotropic behavior in order to obtain materials with desired properties.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7822.

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