Microporous Nanocomposite Material Synthesized by Sol–Gel Processing in the Presence of Cyclodextrins

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Abstract—It is shown that the addition of precursor, tetrakis(2-hydroxyethyl) orthosilicate, that is absolutely soluble in water to a solution of cyclodextrins (CDs) leads to the formation of a hydrogel as a result of sol–gel processes. The synthesis is performed with neither a catalyst nor heating under the conditions that are inapplicable for traditionally employed precursors (tetraethoxy- and tetramethoxy silanes). The occurrence of sol–gel processes is due to the catalytic action of CDs. At the same time, their molecules act as matrix for precipitating polysilicic acids. As a result of hydrogel calcination, xerogels were prepared with micropores and microparticles dimensions of which were determined by the sizes of CD molecules.

INTRODUCTION

Sol-gel processing is currently used widely, because it allows us to synthesize diverse materials with fundamentally new structures and properties [1–6]. The synthesis is performed using the precursor that is commonly represented by titanium, zirconium, aluminum, vanadium, molybdenum, and silicon alkoxides.

To prepare the most widely used materials based of silicon dioxide, the precursor (silane) is added to aqueous solution where it is hydrolyzed. Formed silica acid undergoes the polycondensation to form polysilicic acids $\mathrm{nSiO_2\cdot mH_2O}$. Two main stages are distinguished in this process [1, 3]. First, oligomeric products are formed. They are present in a solution as nanoparticles (sol). At the second stage, sol particles aggregated that is accompanied by the crosslinking with covalent bonds. As a result, the sol is transformed into the gel, i.e., silica gel is formed. Materials prepared by the sol–gel processing are amorphous and do not have a regular structure. To synthesize materials with the preset structural organization, polymers or surfactants that are self-assembled in a solution are employed as organic matrices [3, 5, 7–11]. Polysilicic acids are precipitated in situ on these matrices, thus forming hybrid materials composed of organic and inorganic components. Alternative procedure is proposed [12, 13] involving the performance of sol–gel processes in concentrated (to 40%) solutions of low-molecular-weight compounds, for example, glucose. The subsequent removal of these compounds by washing-off makes it possible to prepare nanocomposites with controlled porosity.

Tetramethoxy- or tetraethoxysilanes usually act as precursors in the synthesis of silica materials [1, 3]. Both compounds are poorly soluble in water. In order to avoid the phase separation, an organic solvent is added to a system. Methanol or ethanol are evolved during the hydrolysis of these precursors. In addition, the sol–gel transition does not occur in aqueous neutral solutions and it is catalyzed by the addition of acid or alkali. The necessity of using organic solvent, the evolution of alcohol during the precursor hydrolysis, and the presence of acid or alkali in a system impose limitations on the performance of processes with the participation of compounds whose state in solution depends on the pH and polarity of a medium [14, 15]. For example, the addition of acid, alkali, or organic solvent can lead to the denaturation and precipitation of a biopolymer that is present in a solution or change the phase state of a surfactant.

To eliminate this obstacle, new precursor, tetrakis(2-hydroxyethyl) orthosilicate (THEOS), that is absolutely soluble in water was proposed [16, 17]. As was shown in the cited works, the characteristic feature of THEOS is its compatibility with polysaccharides. The latter were used not only as a matrix for precipitating polysilicic acids but also as a catalyst of sol–gel processes. This function was performed by various polysaccharides all having linear backbone that determines the structure of synthesized hybrid materials. The structure represented three-dimensional network composed of fibrils formed by macromolecules covered with hydrated silica.

Cyclic polysaccharides (cyclodextrins, CDs) were used in [18–22] instead of linear polysaccharides. Cyclodextrin molecules consist of six, seven, or eight residues of $\alpha$-glucose ($\alpha$-, $\beta$-, and $\gamma$-CDs, respectively).
Since the gelation was not observed in the absence of CDs and catalyst, we concluded that CDs, as well as linear polysaccharides studied previously [16, 17], are capable of catalyzing the sol–gel transition in the systems containing THEOS. As was shown in [17], the catalysis is caused by the formation of hydrogen bonds between the hydroxyls of oligosaccharide molecules and the products of precursor hydrolysis.

The time of gelation depended only on the concentrations of oligosaccharide and precursor, varying from several minutes to several days. Regardless of the fact that α- and β-CDs differ considerably in their solubility (15 and 2 wt %, respectively [26]), significant differences in the processes of gelation were not revealed in their presence.

The maximal amount of β-CD in hybrid materials was 1.5 wt %. When the oligosaccharide concentration in the initial solution approaches 2 wt %, the addition of precursor leads to the precipitation of CD. Note that, even the trace amounts of β-CD in a solution initiated sol–gel processes without a significant decrease in the rate of hydrogel formation. It seems important that the phase separation did not take place upon the gelation even when the amount of CD was equal to tenths of wt %. The hydrogel was formed throughout the system volume as a monolith. The syneresis was observed in systems containing α-CD; however, syneresis was insignificant and no more than 5 wt % solvent was separated.

The gelation rate was greatly affected by the variations in the amount of THEOS in the reaction medium. For example, at the same amount of α-CD, the hydrogel was formed in the presence of 5 wt % of precursor on the seventh day while in the presence of 20 wt %, on the second day.

The dependence of mechanical properties of hydrogels containing 5 wt % of α-CD on the THEOS concentration in the initial solution is shown in a series of plots in Fig. 1. Static viscosity $\eta_0$ (Fig. 1a) and plateau modulus $G_0$ (Fig. 1b) were determined measuring the creep as described earlier [25]. These data characterize the fluidity (viscosity) and elasticity of a material, respectively. Figure 1c demonstrates the values of critical shear stress $\sigma_c$ at which the hydrogel is destroyed and its flow begins; Fig. 1d, the values of corresponding maximal shear strain $\gamma_c$. Parameter $\sigma_c$ is the yield stress used to characterize the mechanical properties of materials [27]. Procedures for determining $\sigma_c$ and $\gamma_c$ are described in more detail elsewhere [25].

The set of rheological data presented in Fig. 1 demonstrates that the mechanical strength of synthesized hydrogels increases with the precursor content in the initial solution. Similar behavior was observed when studying the materials prepared with the use of linear polysaccharides [16, 17]. An increase in the mechanical strength of hydrogels is explained by an increase in the content of polysilicic acids, their molecular mass, and the number of crosslinks in forming gels. Note that static viscosity increases almost linearly with the THEOS concentration (Fig. 1a). Fitting experimental