Study of Cryostructuring of Polymer Systems: 25. The Influence of Surfactants on the Properties and Structure of Gas-Filled (Foamed) Poly(vinyl alcohol) Cryogels


* Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia
** Department of Chemistry, Moscow State University, Vorob’evy gory, Moscow, 119992 Russia
*** Institute of System Analysis, Russian Academy of Sciences, pr. 60-letiya Oktyabrya 9, Moscow, 117312 Russia

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Abstract—Foamed poly(vinyl alcohol) (PVA) cryogels are studied. Such heterogeneous gel composites are formed as a result of the cryogenic treatment (freezing–storage in a frozen state–thawing) of water–PVA liquid foams in the absence and presence of surfactants. It is shown that the addition of ionic and nonionic surfactants to an aqueous PVA solution and its subsequent foaming result in the formation of liquid foam whose stability is lower than that of the foam prepared from an aqueous PVA solution in the absence of surfactant, i.e., surfactants cause a destabilizing effect on the foams containing PVA. Gas-filled PVA cryogels formed as a result of freezing–thawing of such foams contain large (up to ~180 µm) pores (air bubbles incorporated into the matrix of heterogeneous gel). Mechanical and thermal properties of cryogels depend on the nature and concentration of surfactants, as well as on the regime of cryogenic treatment. The rigidity of foamed PVA cryogels prepared in the presence of sodium dodecyl sulfate and cetyltrimethylammonium bromide ionic surfactants is lower and that in the presence of nonionic decaoxyethylene cetyl ether is higher than for equiconcentrated (by the polymer) foamed PVA cryogel containing no surfactant. Microscopic studies and the analysis of obtained images of cryogel structure demonstrate that the effect of surfactant on the morphology of freezing foam can be different, depending on the type of surfactant added to the initial system. This leads to foam-destabilizing effects such as the collapse, deformation, and coalescence of air bubbles; the failure of gel phase structure near the bubble surface; etc. However, the complete disintegration of the foamed structure is prevented by a very high viscosity of the unfrozen liquid microphase of a macroscopically solid sample and by the cryotropic PVA gelation that fixes the structure of partially destroyed foam.

INTRODUCTION

Cryogels of poly(vinyl alcohol) (PVA) are formed due to freezing–thawing of PVA concentrated solutions in water or dimethyl sulfoxide [1]. Typical feature of cryogels is their macroporous structure formed by the polycrystals of frozen solvent; after the melting of frozen solvent, cavities (large pores) filled with a melted liquid are left in a material [2–4]. The sizes of such micropores in PVA cryogels (cryoPVAGs) usually vary from tenths of micrometer to 1–2 µm and depend on the characteristics of PVA (molecular mass and the number of residual O-acyl groups), its concentration in the initial solution, composition of a solution, and, naturally, on the regime of cryogenic treatment [1–6].

Gas-filled (foamed) PVA cryogels (F-cryoPVAGs) belong to little-studied systems; they also possess very large pores with the sizes of tens and hundreds of micrometer. These “supermacropores” are represented by the gas (air) bubbles entrapped in the cryogel matrix. In fact, only one work has been published on the study of F-cryoPVAGs [7]. We demonstrated in this work that the freezing–thawing of foamed water PVA–systems leads to the fixation of liquid foam accompanied by the formation of gas-filled viscoelastic cryogel whose mechanical properties and morphology are determined not only by the aforementioned factors that are “common” for cryoPVAGs, but also by such characteristics of initial foam as its foam ratio and stability. One of the most efficient procedures that affect the properties of foams is the use of surfactants [8, 9]. Therefore, it was important to elucidate how the addition of various types of surfactants (ionic and nonionic) to the initial system will influence the F-cryoPVA structure and properties, as well as to reveal which of new factors related directly to the presence of surfactants in a system, will be of fundamental importance. The answer to these questions is the aim of this work.

EXPERIMENTAL

To prepare F-cryoPVAGs, we used polymer with a viscosity average molecular mass of 69 kDa and the degree of deacetylation of 99% (PVA, 16/1 grade, NPO Azot, Severodonetsk, Ukraine). Prior to the formation of cryogels, polymer was purified as follows. The dry PVA powder was dispersed in sixfold (by weight) excess of deionized water and left to stand at room tem-
perature for three days with a periodic stirring. The supernatant was decanted every day and pure water was added to the precipitate in the amount equal to sampled volume. Then, swollen polymer was separated from free liquid by filtration and pressing through several layers of cotton cloth. The obtained moistened mass containing nearly 24 wt % of dry PVA was stored in a tightly corked vessel.

The following surfactants were employed without additional purification: sodium dodecyl sulfate (SDS, Serva, Germany), cetyltrimethylammonium bromide (CTAB) and decaoxyethylene cetyl ether (Brij-56), two last surfactants were supplied by Aldrich Chemical, US. We used also congo red dye (Aldrich Chemical, US), gelatin (photo grade), phenol (chemically pure), and glycerol (analytically pure), all Reachim, Russia.

To prepare PVA solution, the weighed portion of swollen polymer was dispersed in a required amount of distilled water or surfactant solution so that the content of polymer in a solution was 100 g/l and surfactant concentration fitted the range from 0.25 to 1–5 critical micellization concentration (CMC) of its individual aqueous solution at room temperature. Then, the swollen sample was heated for 20 min (with stirring and avoiding foaming) on boiling water bath until the homogeneous solution was formed. The sample was weighed before and after heating and compensated for the loss of evaporated water. The thus prepared solutions were cooled down to room temperature and afterwards were used to prepare foams, which later were employed to form F-cryoPVAGs.

The foams were prepared using an ENVO MVP-203M high-speed blender (NPO Energiya, V oronezh, Russia). The duration of foaming was determined by the time, which is required to achieve foam ratio \( \beta \) equal to 2 \( (\beta = V_f/V_s, \text{where} V_f \text{is the foam volume and} V_s \text{is the solution volume before foaming, respectively} [8]) \). The stability of liquid foams was estimated by the time intervals elapsed from the end of the foaming of initial solution to the appearance of the layer of transparent liquid at the bottom of a calibrated cylinder filled with the foam (time \( t_1 \)) and to the time when the foam volume decreased twofold (time \( t_{1/2} \)) [8].

The formation of F-cryoPVAGs for measuring their mechanical properties was performed in dismountable duralumin containers with an inner diameter of 15 mm and a height of 10 mm. To study thermal properties, cryogels were formed in transparent polystyrene test tubes with an inner diameter of 1 cm. Two milliliters of liquid foam was poured into a test tube and stainless tubes with an inner diameter of 1 cm and a height of 10 mm. Two milliliters of cryogels were formed in transparent polystyrene test tubes with an inner diameter of 1 cm and a height of 10 mm. To study thermal properties, duralumin containers with an inner diameter of 15 mm were employed to form F-cryoPVAGs.

Fusion temperatures of gas-filled cryoPV AGs were determined as follows. Tightly closed polystyrene test tube with cryogel, whose lower part contained a metal ball, was placed upside down into water bath with a stirrer. Temperature was increased at a rate of 0.4 ± 0.1°C/min. Temperature \( T_f \) at which the ball, passing through the layer of melting gel, fell on the test tube stopper was taken as a fusion temperature.

Shear moduli and fusion temperatures of cryogels were measured for three parallel samples; the preparations were obtained in no less than three independent experiments.

The morphology of prepared cryogels was studied using an AxioLab Pol optical microscope (Carl Zeiss, Jena, Germany). Thin (7–8 µm) F-cryoPVAGs sections for these studies were obtained with an SM-1900 cryomicrotome (Leica, Germany). Then, sections were placed into distilled water and submerged for 10 s into an aqueous 1% congo red solution for the staining. The excess of dye was washed off with water, each section was placed onto a microscope glass, the excess of water was removed with a gauze tampon, one drop of “pouring medium” (solution of 1g of photogelatin in 12 ml of aqueous 50% glycerol solution with 0.2 g of phenol added as a bacteriostatic agent) was placed on the object and pressed with a cover glass. Prior to study, samples were stored in sealed vessels at 4°C.

The analysis and processing of images obtained during the microscopic study of cryogel samples were carried out using inverted black and white negatives. When analyzing the color, we used only its intensity as a measure of the closeness of color variation between gray and black. Gaps (pores) in the F-cryoPVAG structure were considered as the studied objects.

As a result of scanning with a 2000 dpi resolution (an UMAX3000 scanner), we obtained images, which can have the following defects: (a) local broken parts of a film (white points), (b) local distortions (due to possible damage of scanner glass), and (c) distortion in the points of color variations (solid lines with an increased intensity in the points of color variation). To eliminate damaged and distorted parts of scanned images, we used the following image functions (filters) [10]: (a) linear smoothing (linear filtration), (b) an increase in contrast (autocontrast), (c) transformation toward some color range (color discrimination), (d) discretization of color range (a decrease in the number of colors).