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Cryostructuring of polymeric systems. 36. Poly(vinyl alcohol) cryogels prepared from solutions of the polymer in water/low-molecular alcohol mixtures

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ABSTRACT

Poly(vinyl alcohol) (PVA) cryogels are formed via freezing–storing frozen–thawing of concentrated solutions of the polymer. In this study the influence of the additives of the first four members of the series of aliphatic low-molecular alcohols to the initial aqueous PVA solution on the physicomechanical and thermal properties of the resulting cryogels has been explored. Addition of increasing amounts of methanol, ethanol and *n*-propanol were shown to cause a decrease in both the rigidity and the fusion temperature of the respective cryogels, and in the case of *n*-butanol additives the dependence of gel strength *vs.* alcohol concentration turned out to be bell-shaped. It was supposed that one of the basic reasons for such 'deteriorative' effects was the microcoagulation of PVA caused by growing concentration of the low-molecular alcohol in the unfrozen liquid microphase upon the ice crystallization. This assumption was confirmed in the optical microscopy experiments that revealed the formation of PVA microcoagulation zones entrapped in the macroporous cryogel bulk. Such an effect was previously unknown for PVA cryogels. The morphometric analysis (using specially developed algorithms) of the microscopic images of thin sections of such cryogels showed a sophisticated, without obvious direct correlations, pattern of properties–structure dependencies of such heterogeneous cryogels prepared from the solutions of the polymer in water/low-molecular alcohol mixtures.

1. Introduction

It is known, from the beginning of the 1970s [1–3], that cryogenic treatment, i.e. freezing–frozen storage–thawing, of concentrated aqueous solutions of high-deacylated poly(vinyl alcohol) (PVA) produces viscoelastic macroporous gels – so-called PVA cryogels (PVACGs) [4–9]. Nowadays these gel matrices are widely implemented in diverse applied fields, e.g. as various medical materials (artificial cartilages, covers on wounds and burns, gel standards (so-called phantoms) for the verification of MRI and ultrasound apparatus [4–7,10–16]). PVACGs are also applied in biotechnological systems (carriers of immobilized molecules and cells [6,16–20], etc.), in building engineering for the construction in the permanent frost regions [18,21–24], etc.

Besides the gelling agent proper (i.e., PVA) and water, various soluble additives or/and insoluble inclusions (fillers) are usually present in the majority of these systems. Such additives can more or less significantly influence the properties and porous morphology of the respective PVACGs. For instance, adding various low-molecular

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electrolytes – inorganic and organic salts, acids, bases – to the initial PVA solution, which is then subjected to cryogenic processing, causes (depending on the ability of such additives either to inhibit or to strengthen hydrogen bonding) either a decrease in the resulting PVAGs' rigidity and heat endurance, or, alternatively, a significant enhancement thereof. The examples of the former case are the chaotropic electrolytes such as LiCl, NaSCN [25,26], whereas the effects of the latter type are caused by the antichaotropic (kosmotropic) substances like NaF, Na_2SO_4, salts of carbonic acids, etc. [25,26]. Water-soluble additives with surface activity, i.e. surfactants, introduced in PVA solutions prior to their freezing result in significant change in the morphology of macropores in the PVACGs obtained after the system's thawing [27]. The addition of increasing amounts of such polyols as ethylene glycol or glycerol to the feed aqueous PVA solutions yields a gradual decrease in elastic modulus and fusion temperature of the final cryogels, whereas additives of oligoethylene glycols cause the increase in these gels' parameters [28]. The mechanisms of the observed effects in all these cases are rather complicated, since the above indicated additives not only alter the cryoscopic properties of the gelling agent solution (in particular, its freezing point and the ability to supercooling), but also affect the polymer–polymer interactions, thus influencing the PVA crystallization in frozen systems. The latter process gives rise to the formation of microcrystallites that play a role of the junction knots in the 3D supramolecular network of these non-covalent (physical) cryogels [6,7,29–31]. The additives also affect the polymer–solvent interactions, thus changing the solvation extent and, as a consequence, the chain conformation, which, in turn, governs the potential of the pendant OH-groups for the efficient intermolecular contacts [32–34].

For instance, one of the drastic results of the additive-induced influence on the PVA macromolecules can be strong dehydration of chains capable of causing the coagulation of the polymer. However, the influence of such water-compatible amphiphilic coagulants on the PVA cryotropic gelation has not been studied so well. Since such coagulating effect takes place when a certain critical concentration of the precipitant is reached, the following process can occur upon freezing of the initial PVA solution which contains such additive in an amount lower than the critical one. As water is first frozen-out, the boundary concentration of the dehydrating agent is attained, so the proper formation of the respective PVACG is accompanied and also complicated (due to the simultaneous occurrence of several processes) by the coagulation events. Typical representatives of the coagulants–precipitants for the aqueous PVA solutions are the first members of aliphatic alcohol series, namely, methanol (MeOH), ethanol (EtOH) and *n*-propanol (PrOH). These alcohols, on the one hand, are mixed with water unlimitedly, but, on the other hand, are non-solvents for the high-deacylated PVAs [35]. In this connection, the goal of the present study was the systematic exploration of how the listed low-molecular alcohols, as well as *n*-butanol (BuOH), being introduced in the PVA solution prior to its cryogenic treatment, affect the properties and the porous morphology of the resulting PVACGs. An additional incentive of such research was the result of our earlier experiments on the preparation of hybrid organo-inorganic PVA cryogels formed with the additives of tetramethoxysilane, upon the hydrolytic polycondensation of which methanol was liberated and, as it turned out, this alcohol caused a decrease in the rigidity and the heat endurance of the resulting PVACGs [36]. However, the exact reasons for such an effect were remained unclear. Therefore, the second goal of present study was the scientific task to reveal the physicochemical mechanisms responsible for the specific influence of dehydrating agents (the low-molecular alcohols as convenient models) on the formation of PVACGs and their properties.

2. Materials and methods

2.1. Materials

The following substances were used in the work without further purification: poly(vinyl alcohol) with molecular weight of 86 kDa and deacetylation degree of 100% (Acros Organics, USA), methanol (chemically pure grade) was from Reakhim (Russian Federation), 95% ethanol-rectificate (medicinal grade) was from Ferane Co. (Russian Federation), *n*-propanol (analytical grade) was from Dow Chemical Co. (USA), *n*-butanol (pure for chromatography) was from Komponent-Reaktiv Ltd. (Russian Federation). The Congo red dye (Aldrich Chemical Co., USA), gelatine (photo quality), phenol (pure for analysis), glycerol (pure for analysis) (all from Reakhim Co., Russian Federation) were employed as received. All aqueous solutions were prepared using deionised water.

2.2. Preparation of PVA stock solutions

The preparation of PVA stock solutions further used for the fabrication of PVACG samples was performed in accordance with the procedure described earlier [24–27]. In brief, the calculated amount of PVA was suspended in the required volume of water; the mixture was stored for 15 h at room temperature for the polymer to swell. Then the suspension was heated for 1 h under stirring in a boiling water bath for complete PVA dissolution. The sample was weighed before and after heating, and the amount of evaporated water was compensated. Then, the calculated volume of low-molecular alcohol was added with stirring to the polymer solution preliminarily cooled to room temperature; at that the final PVA concentration in all the cases was maintained equal to 100 g/L.

2.3. Cryogenic structuring

The PVACG samples for measuring their physicomechanical characteristics were prepared in sectional duralumin molds with inner diameter of 15 mm and height of 10 mm. The cryogels used for fusion temperature measurement were formed in transparent poly(ethylene) test tubes with inner diameter of 10 mm. The test tubes were filled with 5 mL of the respective polymer solutions, and a stainless steel ball with diameter of 3.5 mm and weight of 0.275 ± 0.005 g was placed on the bottom of each test tube. The containers and the test-tubes were placed into the