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Composite Materials Based on Cryogels

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Abstract

Two methods for the transition of aqueous solutions of polyvinyl alcohol (PVA) from the liquid state of aggregation to the solid state are considered. Freezing an aqueous solution of PVA at a negative temperature and subsequent thawing at a positive temperature result in the formation of rubber-like cryogels. Another way is chemical crosslinking of kinetically individual PVA macromolecules to spatial networks having elastic properties. Sodium tetraborate was used to structure aqueous PVA solutions. The rheological properties of a two-component aqueous solution of polyvinyl alcohol were studied. The study shows that the polymer solution exhibits the properties characteristic of non-Newtonian liquids. The kinetics of gelation of the products of chemical structuring of aqueous PVA solutions with an aqueous sodium tetraborate solution was studied. It is shown that viscosity increases with time as a consequence of chemical interaction. The mechanical properties of carbon-containing composite materials obtained by various methods have been investigated. It has been determined that the most durable materials are those formed by the cryotropic method and those chemically structured after cryogenic treatments. The stress-strain and moisture-resistant properties of carbon materials enable their use as fuel briquettes with a minimum amount of a binder. They can also serve as high-energy fuels for domestic and industrial purposes. The chemical method of structuring a PVA solution can be used for dust control in coal mines.

Keywords: polyvinyl alcohol, sodium tetraborate, carbon, viscosity, cryogel, elastic modulus

INTRODUCTION

Cryogels of polyvinyl alcohol (PVA) are heterophase microporous polymer materials formed as a result of cryogenic treatment (that is, freezing, exposure in the frozen state, and subsequent thawing) of concentrated viscous-flow solutions of the polymer in water. The transition of two-component solutions from the liquid into solid state proceeds without using cross-linking chemical reagents, just due to the formation of hydrogen bonds in the structure of polymeric PVA chains. Cryogels formed under the conditions of solvent crystallisation are thermally reversible but, in contrast to low-molecular compounds, they do not have a fixed phase transition point and melt at a temperature several ten degrees higher than the

temperature of initial aqueous solution structuring (Fig. 1) [1, 2].

Materials obtained on the basis of cryogels are applied in various practical areas, such as oil production, construction, soil science, biotechnology, and medicine [3–5].

The structural elements of cryogels are polyhedral cells with wall thickness from several to several ten nanometres, composed of PVA macromolecules, which render a unique set of physicochemical properties to the cryostructures. At a positive temperature, the internal cavities of the cells are filled with water. Two-component cryogels scatter light as a consequence of the presence of density fluctuations in the polymeric substance in the cell walls and are matted, unlike the transparent PVA solutions. The mechanical prop-

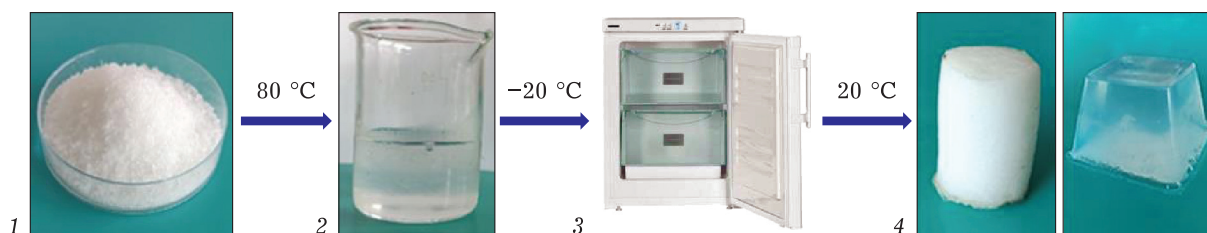


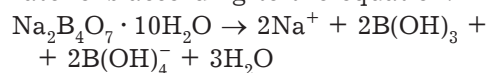
Fig. 1. Cryogel formation: 1 – PVA powder; 2 – aqueous PVA solution; 3 – freezing the aqueous PVA solution in the freezing chamber; 4 – formed cryogels. Here and in Figs. 2–6: – polyvinyl alcohol.

erties of these systems are determined by the nanometre thickness of cryogel framework walls. Deformation under the external stress, for example bending of the polymer framework wall, leads to the elastic (entropy-related) change of the shape of macromolecules, because wall thickness is comparable with the sizes of mobile segments in macromolecules.

In addition to cryogenic action, the aqueous solutions of PVA may be structured also using another approach, involving chemical cross-linking of kinetically individual PVA macromolecules into spatial networks that possess elastic properties. The reagent used in the work to structure the aqueous solutions of PVA (that is, to transform them into non-flowable gels) was low-molecular reagent sodium tetraborate (STB, borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).

The reaction of PVA cross-linking with STB involves the formation of a complex compound composed of one borate ion and four OH groups of PVA. These complexes are formed at a very high rate, which is unusual for gels and complex-forming polymers.

Sodium tetraborate is completely dissociated in aqueous solutions at low concentration with the formation of sodium ions, boric acid, and monoborate ions according to the equation:



The reaction proceeds in two stages: at the first stage, monoborate ion undergoes condensation with vicinal hydroxyl groups of the same polymeric chain with the formation of a six-membered monoborate ring (Fig. 2, a); subsequent intra-chain reaction with other vicinal OH groups leads to the formation of a cross linkage (see Fig. 2, b).

However, it has been assumed that the mechanism of borate cross-linking is ionic. In this case, a cross linkage is formed due to the ionic interac-

tion between borate anion bound to PVA and a chelate sodium cation with PVA (see Fig. 2, c) [6].

Three-component PVA – STD – water gels may be used as instantaneous gel-forming systems exhibiting barrier properties, for example, to provide protection from dangerous chemicals [7, 8], to make water-repellent barriers in hydraulic engineering structures [9, 10].

The introduction of fillers into the polymer cryogel matrix at the stage of its formation provides substantial changes in the structural-mechanical and physicochemical properties of the material, so investigation of these properties is of scientific and practical interest. Carbon particle binding with the above-described polymer and the formation of fuel briquettes [11], as well as instantaneous binding of coal dust for preventing its emission into the workplace air or into the atmosphere, are highly relevant tasks.

The goal of the work was to develop the methods for obtaining filled carbon-containing materials based on cryogels and to investigate their mechanical and physicochemical properties.

EXPERIMENTAL

The initial aqueous solution of the polymer (dispersion medium) was prepared using a PVA sample with a molecular mass about $150 \cdot 10^3$, containing residual acetate groups after polyvinyl acetate hydrolysis at a level not more than 1 % in its structure.

The dynamic viscosity of the two-component PVA – water solution was measured with a rotation viscosimeter Rheotest (Germany) at a temperature of 25 °C within a broad range of shear velocities.

Technical carbon (carbon black), fine powder ($d \sim 0.1\text{--}1 \mu\text{m}$) obtained through isothermal decomposition of hydrocarbons in the absence of

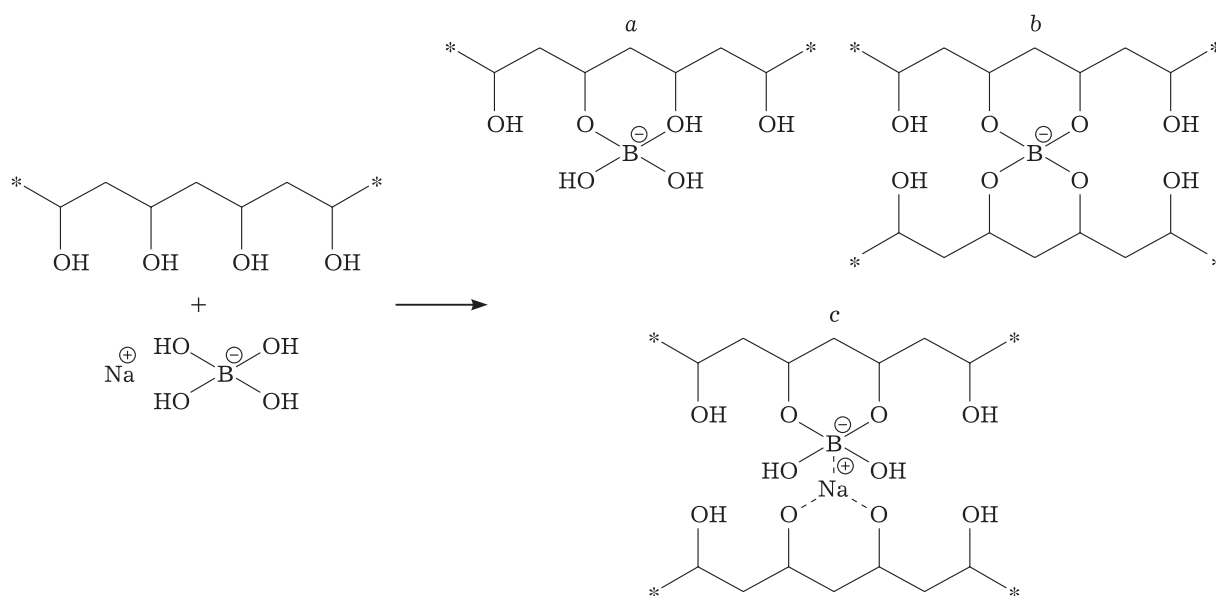


Fig. 2. Complexes formed in the interaction of hydroxyl groups of PVA with borate ions. For designations, see Fig. 1.

oxidisers, was used as a filler. Carbon black of P267-E grade (TU 3811574-86) was used. The fine carbon black particles were impregnated with the aqueous solutions of PVA. Another version involved carbon particle impregnation with the aqueous solution of STB (chemically pure reagent grade, GOST 4199-76), and then with the aqueous solution of PVA.

Some samples were frozen at a temperature of -20°C and thawed at room temperature (20°C). Then the samples were dried at room temperature until complete evaporation of water, which was controlled by means of gravimetry.

For the samples shaped as cylinders, the compression strength was determined for the axial compression with the help of a multipurpose test device Devotrans GP (Türkiye), at the constant velocity of compressing plate 0.1 mm/s.

Water resistance of the obtained samples was determined at room temperature. For this purpose, the samples were placed in distilled water, and mixing was carried out with a magnetic mixer at the bar rotation frequency of 30 r.p.m.

RESULTS AND DISCUSSION

To implement the optimal method of preparing cryogels with the necessary properties, a complete set of data on the rheological features of initial viscous systems with PVA is necessary.

It follows from the dependences shown in Fig. 3 that the concentrated aqueous solutions of PVA are characterised by a feature which is typical

for non-Newtonian liquids: the viscosity of these solutions depends on shear velocity. It should be noted that the viscosity of the polymer solution increases with an increase in its concentration, which hinders impregnation of carbon particles. For this reason, 5 wt. % PVA solution was used in subsequent experiments.

The kinetics of gel formation was investigated in the products of chemical structuring of aqueous PVA solutions with the aqueous STB solution. Results of the measurement of dynamic viscosity changes with time are shown in Fig. 4. One can see that the viscosity of compositions containing STB (curves 2 and 3) is substantially higher than

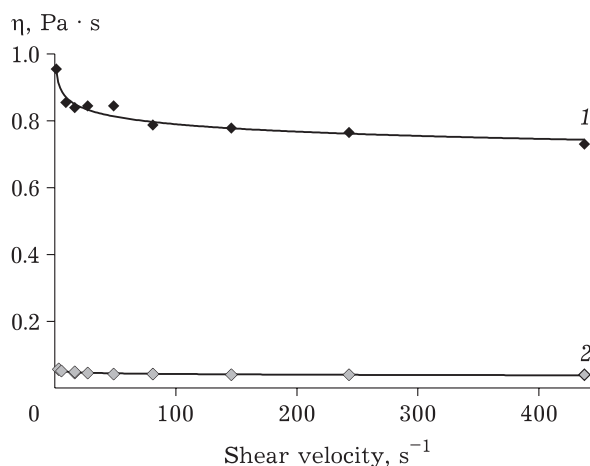


Fig. 3. Dependence of the dynamic viscosity (η) on shear velocity for the aqueous solution of PVA at a temperature of 25°C . The concentration of PVA solution: 10 (1) and 5 wt. % (2). For designations, see Fig. 1.

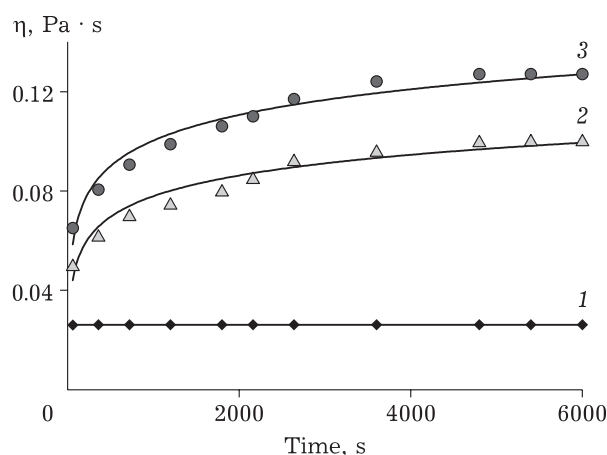


Fig. 4. Dependence of the viscosity of PVA solution ($C_{PVA} = 5$ wt. %, curve 1) and compositions based on it (curves 2 and 3) on time at 20 °C and $Na_2B_4O_7$ concentration 0.0005 (2) and 0.002 mol/L (3). For designations, see Fig. 1.

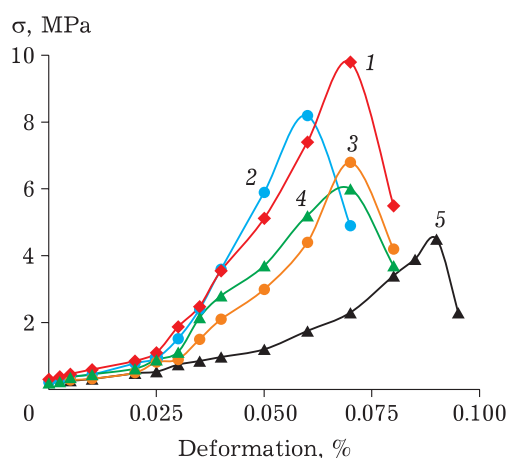


Fig. 5. Dependence of the stress (σ) on deformation for dry carbon materials formed under different conditions: 1 – PVA 1.3 %, coal 98.7 % (cryogel); 2 – PVA 0.663 %, $Na_2B_4O_7$ 0.007 %, coal 99.33 % (cryogel); 3 – PVA 0.663 %, $Na_2B_4O_7$ 0.007 %, coal 99.33 % (gel); 4 – PVA 0.667 %, $Na_2B_4O_7$ 0.001 %, coal 99.332 % (cryogel); 5 – PVA 0.667 %, $Na_2B_4O_7$ 0.001 %, coal 99.332 % (gel). For designations, see Fig. 1.

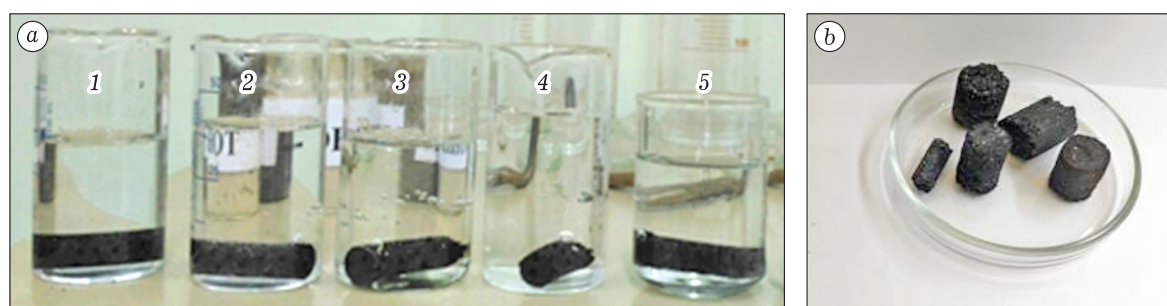


Fig. 6. Carbon materials: a – samples immersed in water (1 – PVA 1.3 %, coal 98.7 % (cryogel); 2 – PVA 0.663 %, $Na_2B_4O_7$ 0.007 %, coal 99.33 % (cryogel); 3 – PVA 0.663 %, $Na_2B_4O_7$ 0.007 %, coal 99.33 % (gel); 4 – PVA 0.667 %, $Na_2B_4O_7$ 0.001 %, coal 99.332 % (cryogel); 5 – PVA 0.667 %, $Na_2B_4O_7$ 0.001 %, coal 99.332 % (gel)); b – fuel briquettes. For designations, see Fig. 1.

the viscosity of PVA solution (curve 1), and the viscosity of these compositions increases with time, which is a consequence of chemical cross-linking.

Carbon-containing composites obtained by cryostructuring of the aqueous PVA solution and cross-linking the polymeric PVA chains by adding STB were then tested for compression strength. The results are presented in Fig. 5.

It follows from the data presented in Fig. 5 that among carbon-containing materials the highest strength is exhibited by the sample formed using the usual cryotropic method without the addition of chemical reagents (see Fig. 5, curve 1). The samples structured using the chemical method become stronger after the freezing-thawing cycle than the samples subjected to chemical cross-linking but without cryogenic action.

In the investigation of water resistance of the obtained materials (Fig. 6, a), all sampled placed in water were observed to conserve their initial shape.

The developed method allows forming strong briquettes from fine coal particles with the minimal amount of binding component to obtain high-energy fuel for domestic and industrial purposes (see Fig. 6, b).

CONCLUSION

Carbon particle binding in the matrix of PVA cryogel matrix by means of physical cryotropic gel formation or through the chemical interaction of STB with PVA solution leads to the formation of a high-strength material. Physical cryotropic structuring of a suspension of carbon-containing

fine particles in a two-component aqueous PVA solution may be recommended to obtain fuel briquettes.

The developed method of coal particle binding may be in high demand at coal mining enterprises for instantaneous coal dust binding. The elastic material obtained using the chemical method after an additional freezing-thawing cycle and drying is characterised by higher strength characteristics than the samples without cryogenic action.

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