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Polyvinyl Alcohol-Based Cryogels for the Oil Industry

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Abstract. The paper presents the results of studies of rheological properties of the initial viscous solutions of polyvinyl alcohol and 'oil-in-water' (O/W) emulsions. It is found that aqueous solutions of polymer and polymer-based colloidal systems have typical non-Newtonian properties. After the freeze-thaw cycle, the viscous liquid systems pass into a solid state of aggregation to form multicomponent cryogels with rubber-like structure. The elastic properties of two-component cryogels consisting of polyvinyl alcohol and water only, three-component compositions formed on the basis of an 'aqueous PVA solution-mineral oil' emulsion, and cryogels containing loose dispersed fillers are investigated. The physicochemical properties of the obtained elastic samples are studied. The prospects of application of cryogels for the oil producing well and road construction are outlined. A comparative analysis of physicomechanical properties of cryogels depending on the nature of the filler is carried out. In order to simulate the real conditions of oil field construction in the permafrost zone, samples of cryogels with solid dispersed fillers pre-wetted with oil are prepared and their mechanical and hydrophobic properties are investigated. Hydrophobic properties of cryogels make it possible to use them as waterproofing layer (membrane) in the construction of the asphalt pavement and insulation of the bottoms and walls of hydraulic structures. Cryogels can be recommended for use as polymer 'pigs' for removal of undesirable deposits in the pipeline during its cleaning or for pipeline pressure testing. In this case, 'batching pigs' are introduced to the boundary between hydrocarbon liquid and water.

1. Introduction

Nowadays, cryotropic nanostructures based on polyvinyl alcohol (cryogels) have become the object of increased interest. Freeze of viscous aqueous solutions of polyvinyl alcohol (PVA), keeping in crystalline state at temperature T < 0 °C for several hours and subsequent thaw within the range of positive temperatures (at T > 0 °C) result in the formation of elastic cryogels (rubber-like bodies). In this case, a transition of two-component solutions occurs from the liquid state of aggregation to the solid state without the use of 'cross-linking' chemical reagents, i.e. due to the enhancement of the intermolecular interaction of the PVA polymer chains [1, 2]. Cryogels formed under conditions of solvent crystallization are thermally reversible but in contrast to low-molecular compounds, they have no fixed phase transition point, hence they are melted at a temperature ($T_{melt.}$), which is several tens of degrees above the temperature of structurization of the initial aqueous solutions (T = 0 °C). Cryogels are non-toxic, environmentally friendly materials used in biotechnologies and medicine [3]. The structural elements of cryogels are polyhedral cells with wall thickness from units to tens of nanometers, formed from macromolecules of polyvinyl alcohol, which give a unique complex of

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physicomechanical properties to cryostructures. The internal cavities of the cells are filled with water. Two-component cryogels scatter light due to the presence of excessive fluctuations in the density of the polymeric substance in the cell walls. Hence, in contrast to transparent PVA solutions, cryogels are opaline bodies. The mechanical properties of such a system are determined by the nanoscale thickness of the cryogel network. Deformation due to the application of external stress, for example, bending of the wall of polymer network, leads to an elastic (entropic) change in the shape of macromolecules, since the wall thickness is commensurable with the values of the moving segments of the macromolecules.

In climatic zones of permafrost, cryogels are used in plugging operations to form blocking screens [4] that prevent undesirable (destructive) filtration of water through dams and bottoms of hydraulic structures. Cryogels are promising materials for the development of new technologies of the construction and repair of producing wells, where, as a result of warm oil seepage, wellhead funnels (sinkholes) are formed, and for cleaning of pipelines. The introduction of modifiers and fillers into the polymer matrix of a cryogel at the stage of its formation changes the mechanical and physicochemical properties of the material; therefore, the study of such properties is of practical interest [5, 6].

2. Experimental section

In order to prepare aqueous polymer solutions, samples of polyvinyl alcohol were used, which contained no more than 1% of residual acetate groups in their structure. Emulsions with hydrophobic properties were prepared by adding predetermined portions of mineral oil to an aqueous PVA solution under vigorous stirring. Mineral oil is a complex multicomponent system consisting mainly of naphthenic and paraffinic hydrocarbons, and aromatic compounds. To form more rigid multicomponent cryogels, fine additives were introduced into an aqueous solution of polyvinyl alcohol: quartz sand or clay (bentonite). To simulate the real conditions of the oil fields, samples of cryogels with bulk fillers pre-wetted with oil were also prepared. Dynamic viscosity (η, Pa•s) of individual liquids (aqueous solutions of polyvinyl alcohol or mineral oil) and their emulsions were measured on a "Rheotest-2' rotational viscometer at different temperatures (T, °C) in a wide range of shear rates (j, s^{-1}).

To manufacture two-component cryogels (polyvinyl alcohol–water), polymer solutions of different concentrations were poured into cylindrical cells and frozen at negative temperature -20 °C. Then solid samples were thawed at room temperature +20 °C. After the freeze–thaw cycle, elastic cryogels were ready for use. Cryogels from emulsions and suspensions were manufactured in cells in a similar way. Figure 1 shows the stages of formation of cryogels of different compositions.

Figure 1. Stages of preparation of filled cryogels: 1 – dry powder of polyvinyl alcohol, 2 – aqueous solution of polyvinyl alcohol, 3 – two-component cryogel, 4 – 'mineral oil in an aqueous solution of polyvinyl alcohol' emulsion, 5 – elastic cryogel containing water, polyvinyl alcohol, and mineral oil.

The degree of hydrophobicity of the surface of oil-filled cryogels was determined by computer video scanning. Droplets of water or oil were applied to the surface of the obtained cryogels and the images of changes in the size of droplets were registered using a microscope. Using the computer program of image processing, the area that a droplet of water takes after acertain time was determined. The formed elastic cryogel samples were deformed (relative strain γ), the elastic stress (P, Pa) arising in the material was measured, and then the modulus of elasticity (G, Pa) using Hooke's formula was calculated. The melting point of cryogels ($T_{melt.}$, °C) was determined by the falling-ball method, detailed in [2]. The thermal insulating properties of cryogels were estimated by the value of the thermal conductivity coefficient (λ, W/K•m), which was determined using the installation with the main working unit consisting of two steel coaxial cylinders. The medium under study was placed into the gap between the cylinders. The value of the thermal conductivity coefficient was calculated using the formula

$$\lambda = Q \ln \langle R1 | R2 \rangle \left[2\pi L t (T_0 - T) \right]^{-1}$$

where R_1 is the inner radius of the large cylinder; R_2 is the outer radius of the small cylinder; Q is the amount of heat transferred from the heated water of the thermostat to the water of inner cylinder; L is the height of the small cylinder; T is the current water temperature in the inner cylinder at some moment in time (t); and T_0 is the temperature of the heat carrier in the thermostat.

3. Results and discussion

The method of rotational viscometry was used to conduct rheological studies of solutions of polyvinyl alcohol and emulsions at different shear rates (j). It was found that these liquids are typical non-Newtonian systems (Figure 2).

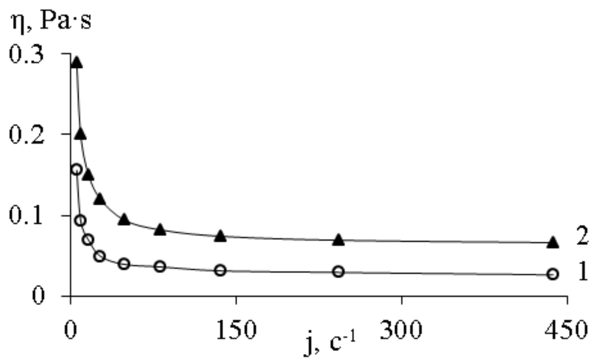

Figure 2. Aqueous solution of polyvinyl alcohol (5 wt%); 2 – 'Oil-in-water'emulsion obtained from an aqueous solution of polyvinyl alcohol (5 wt%) and mineral oil (30 wt%).

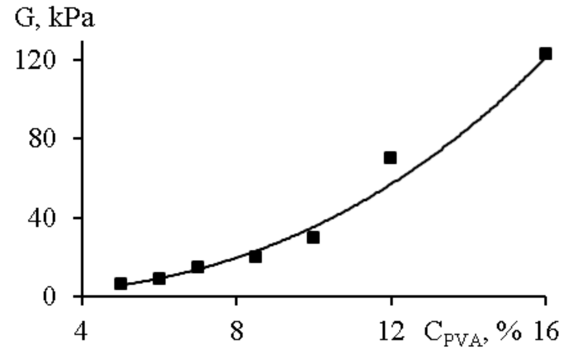

Figure 3. Elastic modulus of cryogels (G) vs the concentration of polyvinyl alcohol (C_{PVA}).

It was experimentally established that the viscosity exponential dependence on temperature (T), described by the Arrhenius–Frenkel–Eyring equation $\eta = A \cdot \exp(E / RT)$, and the viscosity power-law dependence on concentration (C) of the dissolved polymer

$$\eta_P = \eta_S (1 + [\eta] C + k[\eta]^2 C^2 + ...)$$

are characteristic features for aqueous PVA solutions and PVA-based emulsions, as well as for Newtonian liquids. The equation also suggests that a high molecular weight polymer should be used to achieve the maximum viscosity of the solution at the minimum concentration [7].

When studying the viscous properties of PVA solutions in the concentration range of 1–10%, it was revealed that the Weissenberg effect was observed only at a polymer concentration of 5% and higher. It has also been experimentally found that solutions are capable of cryogel forming at a polymer concentration of at least 5%. These experimental facts indicate that a continuous fluctuation network of mutually entangled macromolecules exists already in the initial solutions with such a concentration. The presence of this network is confirmed by the manifestation of the Weissenberg effect.

By giving experimentally the strain (γ) to formed cryogel samples and by measuring the elastic stress (P) arising in the material, the elastic modulus (G) was calculated using the Hooke formula $P = G \cdot \gamma$. It follows from Figure 3 that the modulus of elasticity of polymer bodies increases noticeably from 10 to 120 kPa with an increase in the PVA concentration of the samples from 5 to 16%.

Studies of the effect of the number of freeze-thaw cycles (n) on the elastic properties of two- and multicomponent cryogels revealed an increase in the elastic modulus after each subsequent cycle. The most elastic properties were observed for samples containing mineral oil in the polymer matrix of the cryogel (Figure 4).

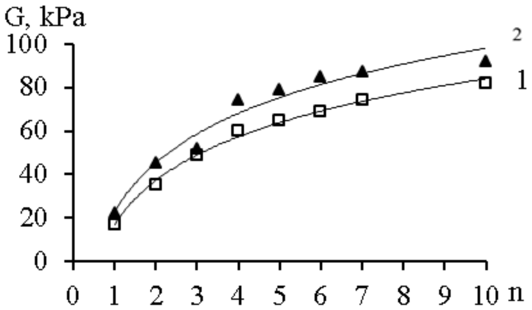

Figure 4. Elastic modulus of the cryogel (G) vs the number of freeze-thaw cycles (n). The composition of systems: 1. PVA – 10%; 2. PVA – 10%, and mineral oil – 30%.

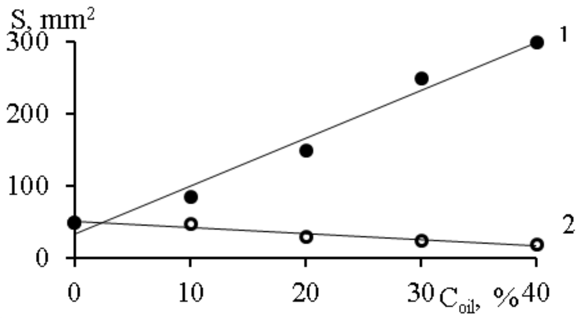

Figure 5. Areas of droplets of oil (1) and water (2) on the surface of cryogels vs the content of mineral oil present in them.

It was found that due to the spreading of a drop of oil, the degree of hydrophobicity of cryogels filled with mineral oil increases significantly with an increase in the content of hydrocarbon filler, while the area of a droplet of water decreases (Figure 5).

The samples with the lowest content of polyvinyl alcohol, which is the main structure-forming component, have the greatest use or economic value for application of cryogels as structural materials. Therefore, in subsequent experiments, the use was made of a 5% aqueous PVA solution doped with various additives increasing the rigidity of cryogels: inorganic salts, glycerin, quartz sand, clay (bentonite), and cement. All these ingredients significantly increase their elastic moduli of the samples (Figures 6-8 and Table 1). To simulate the real conditions of the oil fields, samples of cryogels with finely dispersed fillers previously soaked in oil were prepared from suspensions. Then, the elastic moduli (G, kPa) and thermal conductivity coefficients (λ, Wt / Km) of the samples were measured.

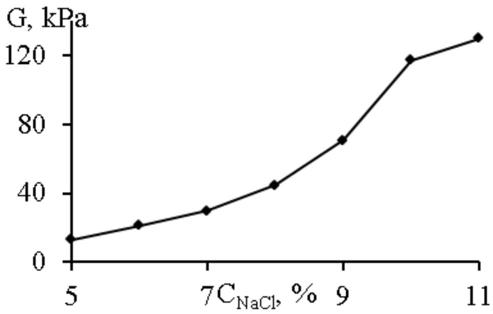

Figure 6. Elastic modulus of a cryogel (G) containing 5% PVA vs the concentration of sodium chloride (C_{NaCl})

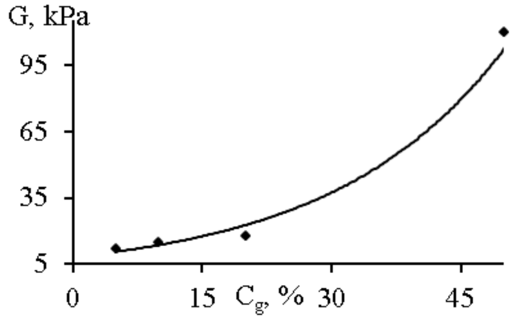

Figure 7. Elastic modulus of a cryogel (G) containing 5% PVA on the concentration of glycerol (C_g, %)

It is evident from Table 1 that the elasticity of these samples substantially exceeds the elasticity of simple two-component cryogels (PVA-water) even in the presence of hydrophobic fillers (sand, bentonite, and cement, pretreated with oil). It is known that the coefficient of thermal conductivity of water is equal to λ_B = 0.62 Wt/Km. The coefficients of thermal conductivity of wet soil (sand, clay, cement-sand solution, etc.) have even higher values in the range (1-2) Wt/Km. The layers of the polymer matrix between the fine particles of the filler perform a 'damping' function and reduce the thermal conductivity of the cryogel by half as compared with water. Thus, the excellent mechanical and thermal insulation properties of cryogels make them advisable to use for the construction of producing oil wells, in the mouth of which paraffin deposits are often observed when cooling the oil coming to the surface.

Table 1. Composition and properties of filled cryogels.

No.	Composition of the initial solution for cryogel formation, %	Properties of cryogels	
		G, kPa	λ, Wt/Km
1	Aqueous PVA solution (5%)	10	0.33
2	Aqueous PVA solution (10%)	40	0.31
3	Aqueous PVA solution (10%) + sand	775	0.35
4	Aqueous PVA solution (5%) + sand	629	0.36
5	Aqueous PVA solution (10%) sand + oil	270	0.34
6	Aqueous PVA solution (5%) sand + oil	150	0.35
7	Aqueous PVA solution (10%) + bentonite	587	0.34
8	Aqueous PVA (5%) + bentonite	465	0.35
9	Aqueous PVA solution (10%) bentonite + oil	589	0.33
10	Aqueous PVA solution (5%) bentonite + oil	345	0.34
11	Aqueous PVA solution (10%) + cement	963	0.37
12	Aqueous PVA solution (5%) + cement	885	0.38
13	Aqueous PVA solution (10%) cement + oil	677	0.34
14	Aqueous PVA solution (5%) cement + oil	416	0.35

Transportation of oil through pipelines is accompanied by the deposition of the mechanical micro impurities and water, as well as asphaltenes, resins, and paraffins. These deposits accumulated in low-lying pipeline sections reduce the effective cross-sectional area of the pipeline and increase the energy consumption of the pumping. To remove undesirable deposits, mechanical scrapers are usually used, which have a significant drawback of inability to pass through local pipe resistances (line bends, restrictions/expansions, etc.). It is possible to solve this problem by means of viscoelastic polymer 'pigs', which are introduced into pipelines when their periodic flow testing for the purpose of separate transfer of dissimilar liquids. These 'batching pigs' introduced at the boundary between the hydrocarbon fluid and water, perform the separating function of the working body during such operations.

In most cases, source material for the manufacture of viscoelastic gels fit for use in pipelines with sections of variable diameter, is polyacrylamide. Another way to form polymer 'batching pigs' may be the above-described cryotropic gelling of polyvinyl alcohol solutions. To strengthen the cryogel, glycerol (50%) was additionally introduced into the initial binary composition of the aqueous PVA solution (5%). The resulted cryogel of a density 1200 kg/m^3 had a significantly higher modulus of elasticity G = 110 kPa compared with the modulus of elasticity G = 10 kPa of the cryogel based on an aqueous solution of PVA (5%). The advantage of the three-component sample is also its resistance to dehydration, which allows it to be stored in the open air without visible changes over a long period of time.

To test the technological properties of the cryogels obtained, a laboratory setup was assembled, which included the following units connected in series: a pressure pump, a pressure gauge for recording differential pressure ΔP, a polymer 'pig' injecting chamber, and a pipeline model consisting of three segments: an U-shaped tube, spiral-shaped and straight sections. Similar diameters of the injecting chamber and the segments of pipeline were equal to $4 \cdot 10^{-3}$ m. In technologies for cleaning of pipelines and separate pumping of liquids using a 'batching pig', the L/R ratio between the length L of the pig and its radius R is of great importance. Therefore, we formed gels in two chambers having the same radius $R = 2\cdot10^{-3}$ m and different lengths $L_1 = 8\cdot10^{-2}$ m and $L_2 = 18\cdot10^{-2}$ m. The spiral-shaped and straight sections were filled with gasoline. Metal filings, simulating mechanical deposits in pipelines were put into the U-shaped tube. During the experiment, water was pumped into the injecting chamber. Due to the immobility of the 'batching pig', the injection of the first portions of water was accompanied by an increase in pressure up to a certain threshold limit value ΔP. Upon reaching this threshold value, the polymer 'pig' was separated from the pipe wall and its further uniform motion along the pipeline segments occurred under the influence of some constant pressure drop ΔP_{pipe}.

The shear stress for the separation from the wall (τ_1) and shear stress for uniform motion of cylindrical cryogel 'pigs' having binary and ternary compositions (τ_2) along the pipe were calculated by the formula $\tau = (R/2L)\cdot\Delta P$. The results of the experiments are presented in Table 2.

Table 2. Hydrodynamic parameters of the polymer 'pig' motion in pipes of various geometries.

No. of gel pig injecting chamber	L/R	Binary composition		Ternary composition	
		τ_{pig}, Pa	τ_{pipe}, Pa	τ_{pig}, Pa	τ_{pipe}, Pa
1	40	380	200	1250	290
2	90	1100	450	2160	870

When passing of cryogel 'pigs' through the model pipeline system, a complete removal of mechanical impurities from the pipeline body and the absence of a zone of mixing of water and hydrocarbon fluid were observed. After analyzing the results of laboratory experiments (Table 2), we tried to predict the potential industrial use of PVA-based cryogels. It can be expected that the a polymer 'batching pig', for example, 10 m long and 1.2 m in diameter, will separate from the pipe wall at an excess pressure not exceeding $1\cdot10^5$ Pa (ΔP <1 kg/cm^2). Hence, low values of the pressure drop, which is necessary for the separation of the polymer 'pig' from the pipe wall exclude the possibility of blocking the tube side and creating an emergency situation.

4. Conclusions

Introduction of a hydrophobic ingredient to the polymer matrix of cryogel at the stage of its cryostructuring is accompanied by the appearance of water-repellent properties of the material.

Cryostructuring of a suspension of loose inorganic material (sand or clay) in a solution of polyvinyl alcohol could be used in regions of permafrost in road and oil well construction.

Cryogels can be recommended as elastic 'batching pigs' for cleaning of pipelines from undesirable impurities.

Acknowledgments

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