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Effect of an Oxidized Polymeric Petroleum Resin on the Properties of Cryogels

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Abstract

The rheological properties of a two-component aqueous solution of polyvinyl alcohol (PVA), as well as emulsions consisting of water, PVA and hydrophobic filler, have been studied. The dispersed phase of the emulsions was transformer oil (TO) or polymeric petroleum resin (PPR), and the dispersion medium was an aqueous solution of PVA. To increase the adhesion of the PPR to the soil particles, the resin was pre-oxidized with hydrogen peroxide H_2O_2 to produce an oxidized polymeric petroleum resin (OPPR). After the freezing/thawing cycle, cryogels were formed from liquid systems and their mechanical, thermal, and physicochemical properties were studied. It has been established that cryogels containing TO have more elastic properties as compared with two-component cryostructured systems (PVA – water), but have less elasticity than cryogels containing PPR. The latter are also characterized by better thermal insulation properties compared to two-component cryogels. A particular feature of cryogels filled with OPPR is their hydrophobicity. It was revealed that after the soil was impregnated by a polymer emulsion with OPPR and a cryogel was formed subsequently after a freezing/thawing cycle, a water-proof shield was formed. Materials based on cryogels with hydrophobic properties, filled with OPPR, are promising and can be recommended for practical use in the oil and construction industry.

Key words: polyvinyl alcohol, polymer solution, polymeric petroleum resin, viscosity, cryogel, hydrophobicity, modulus of elasticity

INTRODUCTION

The transformation of the secondary products of petrochemical industry into useful materials is one of the problems in the development of modern energy- and resource-saving technologies [1]. Petrochemical works are among the most energy-consuming plants where many wastes and by-products are formed along with the target products. These by-products include polymeric petroleum resins (PPR). They are synthesized through oligomerization of unsaturated compounds which are present in the products of the high-tempera-

ture pyrolysis of hydrocarbon raw material during the production of lower olefins.

It is known [2, 3] that refrigeration of viscous-flow aqueous solutions of polyvinyl alcohol (PVA), their storage in the crystalline state (at $T < 0$ °C) for several hours, followed by thawing within the positive temperature range (at $T > 0$ °C), leads to the formation of elastic cryogel (rubber-like agent), that is, a transition of the two-component solutions from the liquid aggregate state into a solid-like state is observed without any linking chemical reagents. Cryogels formed under the conditions of solvent crystallization are thermally

reversible but melt at a temperature several ten degrees higher than the temperature of solution structurization. At present, cryostructured PVA has won broad application in medicine, biotechnologies and food industry because it is non-toxic and ecologically safe [2, 3]. It may be used in oil mining and transportation [4], in making moisture-proof screens to prevent unfavourable filtration of water through the walls and bottoms of hydraulic structures [5, 6], and in industrial and road construction [7].

The introduction of modifiers and fillers into the polymeric cryogel composition causes substantial changes of structural-mechanical, thermal and physicochemical properties of the material [8]. Cryogels with hydrophobic fillers conserve their mechanical and physicochemical characteristics for a long time under substantial temperature drops in humid environments. The substances used as hydrophobic fillers are most frequently mineral and vegetable oils, soot and so on [9–12]. In the present work, we used a mineral oil of petroleum origin (transformer oil, TO) and PPR as hydrophobic fillers. PPR is an oligomer obtained from the monomers of unsaturated hydrocarbons which are residual products of the industrial pyrolysis of petrol [13–15]. The use of PPR instead of emulsified mineral oil in the cryogel matrix is explained by the fact that the products made of polymers are characterized by plasticizer ponding, that is, spontaneous release of this ingredient from the internal volume of a body onto its surface. The use of PPR, with its larger molecular mass ($M \sim 500\text{--}3000$ a.m.u.), instead of the mineral oil (a mixture of low-molecular hydrocarbons with molecular masses within the range $M \sim 100\text{--}500$ a.m.u.) [14, 15] causes a substantial deceleration of the diffusion of large molecules to the surface of the polymeric matrix composed of structured PPR molecules, which causes a substantial improvement of the performance characteristics of moisture-proof screens.

The goal of the work was to develop the formulation and to study the properties of the moisture-proof composition based on cryogels, possessing high adhesion to ground and exhibiting hydrophobic properties.

EXPERIMENTAL

To prepare the initial aqueous solution of the polymer, which served as the dispersion medium for the direct emulsion, we used a PPR sample

with the molecular mass $M \approx 150 \cdot 10^3$ a.m.u. containing not more than 1 % of residual acetate groups in its structure.

Hydrophobic fillers TO and PPR were used as the internal phase. The polymeric petroleum resin contained mainly unsaturated hydrocarbons of the aromatic series (styrene, α -methylstyrene, dicyclopentadiene, etc.) – up to 70 %. It should be stressed that PPR is soluble in nonpolar solvents and insoluble in water and polar solvents. In order to enhance the adhesion of PPR to ground particles, it was oxidized preliminarily with H_2O_2 , thus increasing the fraction of oxygen-containing groups: carboxylic, hydroxyl and epoxy – in the resulting oxidized products. Petroleum solvent was used as a solvent to make the solutions of oxidized polymeric petroleum resins (OPPR). Unless otherwise stated, H_2O_2 concentration was 3 %.

To stabilize the direct emulsion obtained from the aqueous solution of PVA and TO (or a solution of PPR), we used neonol AF₉₋₁₂ as a surfactant. This oxyethylated alkyl phenol [16] based on propylene trimer is a technical mixture of polyethylene glycol ethers of monoalkyl phenols with the composition $C_9H_{19}C_6H_4O(C_2H_4O)_nH$.

The emulsions were prepared with the help of a rotor dispergator IKA ULTRA TURRAXT18. Dispersing time was 5–10 min, the frequency of rotor revolution was 15 000–18 000 r.p.m.

Measurements of the dynamic viscosity of oil, as well as the solutions (PVA, PPR and OPPR) and their emulsions, were carried out with a rotary viscosimeter Reotest at different temperatures within a broad range of shear rates.

To obtain two-component cryogels (PVA – water), the polymeric solutions of different concentrations were poured into cylindrical cells and frozen at a temperature of -20 °C [12]. Then the samples were unfrozen at the room temperature (20 °C). After a cycle of freezing – thawing, elastic cryogels were obtained. A similar method was used to obtain cryogels from emulsions.

Deformation was imparted to the formed elastic samples, and the strain arising in the material was measured. Then the modulus of elasticity was calculated according to Hooke's law.

The temperature of cryogel melting was determined using the drop ball method described in [17, 18]. For this purpose, cryogel sample was placed in a cylindrical vessel on the bottom of which there was a ball made of stainless steel. The glass vessel with the cryogel was sealed and put into the drying oven at the initial temperature of 50 °C, then temperature was increased

with a step of 1 °C. The samples were kept at each temperature point for not less than 15 min. The temperature at which the ball passing through the layer of melting gel fell on the vessel bottom was recorded as the melting temperature.

Heat-insulating properties of cryogels were evaluated on the basis of the coefficient of thermal conductivity. This coefficient was determined using a set-up with the main working unit made of two steel coaxial cylinders. The medium under investigation was placed in the gas between the cylinders [19, 20].

Waterproofing properties of cryogels filled with OPPR were evaluated on the basis of the limiting pressure gradient in the laboratory set-up [21]; the blocking screen filled with ground (sand or clay) has to bear that pressure. The degree of sample swelling in contact with water was determined from the amount of absorbed water using the gravimetric method. The degree of cryogel swelling α was calculated using the equation $\alpha = [(m - m_0)/m_0] \times 100 \%$, where m_0 is the mass of the initial cryogel sample; m is the mass of swollen cryogel.

The interfacial angle Θ of the emulsions was determined using the KRUSS DSA25 instrument.

The degree of hydrophobicity of cryogel surface was measured by means of computer video scanning: a drop of water was placed on the surface of the resulting cryogel, and the changes of the drop size were recorded with the help of the microscope. The area occupied by the drop after a definite time interval, necessary for the equilibrium to be established, was determined with the help of the computer image processing software. The degree of the relative hydrophobicity of the cryogel β was calculated using the equation: $\beta = [(S_0 - S)/S_0] \times 100 \%$, where S_0 is the area of water drop on the surface on the two-component cryogel; S is the area of the water drop on the surface of cryogel filled with the resin.

RESULTS AND DISCUSSION

When forming the initial multicomponent emulsions for their subsequent cryostructuring, it is necessary to keep in mind the fact that an increase in the concentration of PVA in the dispersing medium or an increase in the content of hydrophobic filler promotes an increase in the viscosity of the colloid system [11]. The viscous properties of the medium due to intermolecular interactions not only prevent the flow of liquids

but also hinder mechanical dispersing of the hydrophobic phase. Because of this, to obtain finely dispersed and stable emulsions, it is necessary to control their rheological characteristics which strongly affect the characteristics of the final products after cryostructuring (Fig. 1).

The introduction of the dispersion of liquid hydrophobic fillers into the aqueous solution of PVA is accompanied by a sharp increase in the viscosity of the system and the noticeable manifestation of the non-Newtonian properties in direct emulsions (see Fig. 1).

The maximal density is demonstrated by cryogels containing the micro-drops of OPPR due to the increased intermolecular interaction between the components of the system formed after dispersing the modified polymeric petroleum resin with polar groups in the aqueous solution of PVA (Fig. 2).

The data shown in Fig. 2 also confirm a characteristic feature of cryogels which is in an increase in the modulus of elasticity with an increase in the number of freezing-thawing cycles [2]. This feature makes the industrial application of cryogels in the northern latitudes of Russia promising.

As indicated above, the presence of TO micro-drops in the cryogel determines weak binding of oil components with the polymeric matrix. As a consequence, the diffusion of nonpolar and mobile TO molecules of small size proceeds from the internal volume of the sample to its outer surface. So, cryogel loses its elastic and hydrophobic properties. Quite the contrary, larger PPR molecules

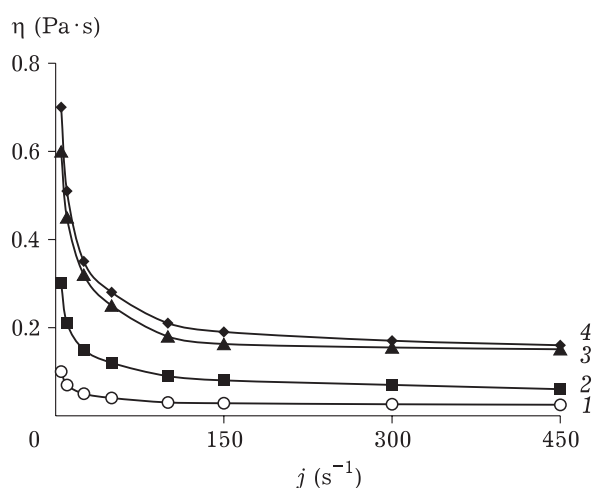


Fig. 1. Dependence of dynamic viscosity η on shear rate j : 1 - aqueous solution of PVA; 2 - emulsion of transformer oil (300 kg/m³) in the solution of PVA; 3 - emulsion of PPR (300 kg/m³) in the solution of PVA, 4 - emulsion of OPPR (300 kg/m³) in the solution of PVA. In all cases, the density of PVA solution is 50 kg/m³.

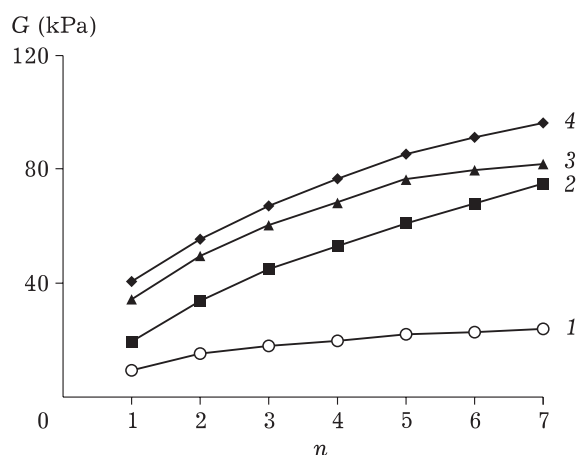


Fig. 2. Dependence of the modulus of elasticity G of the cryogels of different compositions on the number of freezing – thawing cycles (n): 1 – PVA (50 kg/m^3); 2 – TO (300 kg/m^3)/PVA (50 kg/m^3); 3 – PPR (300 kg/m^3)/PVA (50 kg/m^3); 4 – OPPR (300 kg/m^3)/PVA (50 kg/m^3).

are forced out from the internal volume of the cryogel much slower. However, they have another disadvantage, which is manifested at the stage of emulsion preparation. The emulsion of PPR in the aqueous solution of PVA is very unstable and gets destroyed very rapidly if the solution does not contain a corresponding surfactant in a definite concentration. This hinders subsequent cryostructuring of the emulsion and the formation of cryogels with stable properties. Because of this, we carried out preliminary oxidation of PPR molecules which contain unsaturated bonds in their initial structure. Oxidation was carried out using the solutions of H_2O_2 with different concentrations. Oxidized PPR with the polar functional groups (hydroxyl, carboxylic etc.) was thus prepared.

The results of the titrimetric analysis of the resulting OPPR are shown in Fig. 3. These results confirm the disappearance of some fraction of double bonds and the appearance of oxygen-containing groups.

PPR species modified through oxidation acquire surfactant properties, and a stable emulsion is formed, without the addition of any additional surfactant, after dispersing in the aqueous solution of PVA. Due to the presence of polar groups, OPPR macromolecules are strongly bound to the polymeric matrix of the formed cryogel, which presents ponding of the hydrophobic ingredient.

From the practical viewpoint, in order to obtain cryogels, it is reasonable to use the polymeric component in the smallest amounts in the initial emulsion, that is, to form cryogels from the systems with the minimal PVA concentration $\sim 50 \text{ kg/m}^3$,

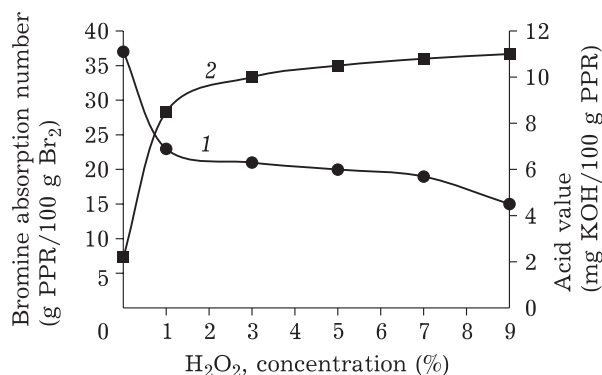


Fig. 3. Dependence of the bromine absorption number (1) and acid value (2) for OPPR on the concentration of the used oxidizer (H_2O_2).

below which cryostructuring is not observed in the aqueous samples of the polymer sample with the above-mentioned molecular characteristics [2, 12]. The results of the studies of mechanical and thermal properties of cryogel samples formed after one freezing-thawing cycle are presented in Table 1. One can see that the introduction of OPPR into the polymeric cryogel matrix is accompanied by an increase in the elasticity of structured systems and a slight decrease in their melting temperature, as well as an improvement of thermal insulating properties by a factor of 1.5 in comparison with the two-component cryogel obtained from the PVA solution (50 kg/m^3). Cryogel samples of any composition are insoluble in water and practically unswelling. A remarkable feature of cryogels filled with OPPR is their hydrophobicity. After the deposition of a drop of water on the surface of these cryogels, a decrease in the wetting area in comparison with cryogels without fillers is observed (see Table 1). The existence of water-repellent properties in cryogels with OPPR allows us to recommend them as a material for water proofing.

Cryostructures with the addition of solid dispersed particles having the hydrophilic nature (such as clay or quartz sand particles) are also of practical interest. It may be expected that in this case the presence of OPPR possessing high adhesion ability in comparison with PPR will enhance the affinity of the filler in the emulsion to the surfaces of solid dispersed particles with hydrophilic characteristics. Indeed, with an increase in the concentration of the aqueous solution of H_2O_2 used as

TABLE 1

Stability of emulsions and the properties of cryogels formed from these emulsions

Composition of the initial system, phase/medium	t , h	E , kPa	T_m , °C	λ , W/(K·m)	α , %	β
PVA solution (50 kg/m ³)	–	11	70	0.34	4	0
OPPR (100 kg/m ³)/PVA (50 kg/m ³)	5	25	69	0.24	3	45
OPPR (200 kg/m ³)/PVA (50 kg/m ³)	24	34	67	0.22	2	55
OPPR (300 kg/m ³)/PVA (50 kg/m ³)	48	40	65	0.20	2	64

Note. t is the time of emulsion stability; E is the modulus of sample elasticity; T_m is melting temperature; λ is the coefficient of thermal conductivity of cryogels; α is swelling degree; β is the degree of sample hydrophobicity.

TABLE 2

Interfacial angle of glass surface wetting by the emulsion composed of OPPR/PVA

Concentration of the solution of H ₂ O ₂ , %	0	1	3	5	7	9
Interfacial wetting angle Θ , deg	60	55	49	44	40	37

TABLE 3

Composition and properties of cryogels filled with friable materials

Composition of initial system	Cryogel properties	
	Modulus of elasticity (E), kPa	Coefficient of thermal conductivity (λ), W/(K·m)
PVA solution (50 kg/m ³)	11	0.34
Sand/PVA solution (50 kg/m ³)	629	0.36
Sand/OPPR (200 kg/m ³)/PVA (50 kg/m ³)	550	0.35
Bentonite/PVA solution (50 kg/m ³)	465	0.35
Bentonite/OPPR (200 kg/m ³)/PVA (50 kg/m ³)	425	0.34

the oxidizer, and the corresponding increase in the degree of PPR oxidation, the interfacial angle of wetting the glass plate decreases (Table 2).

The formulations of initial liquid compositions and the results of measuring the mechanical and thermal characteristics of cryogels made of them, tightly filled with friable materials – clay (bentonite) and quartz sand – are presented in Table 3. One can see that the rigidity (elasticity) of the samples of suspended cryogels increases sharply in comparison with the two-component cryogel (PVA – water), while the heat conductivity coefficient remains practically unchanged.

Hydrodynamic tests that were carried out in the laboratory set-up for the investigation of liquid filtration through porous and friable materials allowed us to establish that a screen impermeable for water is formed after impregnation of these materials by the polymeric emulsion with OPPR and the formation of cryogel from this emulsion after the freezing-thawing cycle. the limiting pressure gradient up to which no filtration of water occurs through the screen of cryo-

gel with dispersed rock is 1.2 MPa/m for sand and 2.6 MPa/m for clay.

CONCLUSION

Cryostructuring of the direct emulsions composed of the aqueous solution of PVA and PPR allows obtaining cryogels with specific mechanical, thermal and adhesion properties. The formed cryogels with hydrophobic properties, filled with OPPR, are promising and may be recommended for practical use as waterproof screens for walls and bottoms of hydraulic structures, as well as for waterproofing for road construction to prevent the destruction of asphalt surfacing as a result of seasonal temperature variation.

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