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Cryogels and Gels for Advanced Technological Processes in Coal Industry

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Abstract

The rheological (structural-mechanical) properties of gel-forming compositions, gels and cryogels based on polyvinyl alcohol, as well as the compositions developed at the Institute of Petroleum Chemistry SB RAS, which are promising from the viewpoint of preventing endogenous fires and intensifying methane release during interval hydraulic fracturing of coal seams, have been studied. The amplitude and kinetic dependences of the elastic modulus (G'), loss modulus (G'') and complex viscosity were obtained in the oscillatory mode using the rheometer with controlled deformation for the compositions differing from each other in the ratio of components at different temperatures. It has been shown that the gel starts to form already at the moment of component mixing, and the elastic properties of the forming structure predominate ($G' > G''$). The values of gelation points were determined. It is found that with an increase in crosslinker concentration, the strength of the resulting structure increases, and the time of gel formation decreases. As the temperature decreases, the strength of the resulting structure also increases. In the static mode of sample deformation, it is established that the gel is further stabilised after the freeze-thaw cycle. The developed composition has strength properties and good adhesion to the surface of coal. It can be used to protect coal mine faces from spontaneous combustion and as a protection from coal dust on technological roads. The change of the deformation-compression dependence under constant load on time for gel and cryogel was studied. It has been established that under a constant stress of 7 kPa, gel deformation reaches 25 %, while cryogel deformation is 15 %, that is, the elastic properties of the composition increase after a freeze-thaw cycle. In this regard, it is preferable to carry out the work at sites in the autumn and spring time.

Keywords: gel, cryogel, elastic modulus, oscillatory rheometry, polyvinyl alcohol, coal, ecology, hydraulic fracturing

INTRODUCTION

The studies of gel-forming fluids for hydraulic fracturing are carried out mainly in China, USA and Australia [1–5]. Along with traditional fluids based on crosslinked guar gum, the possibilities to use the new types of water-soluble polymers of cationic and anionic types with the addition of zwitterionic surfactants are under investigation. Promising, though underinvestigated, are gel-forming polymer solutions with the upper and lower dissolution temperature points, possessing the ability to be reversibly transformed into gel under temperature changes.

This feature of gel-forming solutions is in high demand in the coal mining industry, as under definite geological conditions of coal bedding endogenous fire events can burst out with an increase in oxygen access to coal during mining. Different methods of fire fighting are applied, depending on the conditions under which combustion proceeds. The most widespread method of suppressing endogenous fire is considered to be water injection into a coal bed; however, this causes its deformation and brings about the danger of steam discharge. The injection of liquid inhibitors into a coal bed is efficient only if the exact position of fire seat is known. The deposition of insulating material to block oxygen access to the fire seat and to minimise the evolution of hazardous substances into the atmosphere forms the most promising method. Development of the materials and new methods to prevent coal self-ignition in open coal mines appears to be the relevant task motivating the research in this direction. At the Institute of Petroleum Chemistry SB RAS (IPC SB RAS), the formulations of gel-forming compositions and cryogels to be deposited on coal surface have been developed, providing the formation of a protective film limiting the access of oxygen. These systems possess pronounced structural-mechanical properties that can be characterised by rheological measurements. From the viewpoint of non-destructive action on the forming structure during measurement, it is preferable to use the methods based on the oscillatory motion of a test body, such as oscillatory rheometry or oscillatory viscometry [6–8].

Cryogels and gels combine a set of useful properties: the ability to transfer the propping agent in the suspended state, to simplify the formation of cracks and disintegration of coal seams due to adsorptive strength loss, known in Russia as Rehbinder effect, and to promote methane filtration, which is especially important for the implementation of interval hydraulic fracturing technologies for the preliminary seam degassing. In this case, several physicochemical phenomena exhibit synergism: thermally reversible phase transition polymer solution – gel, sedimentation stability of the propping agent in the gel, the phase permeability of gel for methane, adsorption-caused reduction of coal strength, simplifying the formation of cracks.

The goal of the work was to study the rheological properties of gel-forming compositions, gels and cryogels, which are promising from the viewpoint of fighting endogenous fires and intensifying coal seam degassing [9].

EXPERIMENTAL

In the work, we studied gel-forming compositions prepared from the gels and cryogels of polyvinyl alcohol (PVA) with the molecular mass ~$150 \cdot 10^3$ and the alkaline composition IPC-PRO based on the inorganic buffer system and a polyol [10, 11]. The gel-forming composition forms a gel as a result of intermolecular interaction of the aqueous solution of PVA (gel former) with IPC-PRO (crosslinker) at a temperature of 0–20 °C, and then the gel is transformed into cryogel in cyclic freezing-thawing processes. In the experiments, the composition IPC-PRO was diluted with distilled water at a ratio of 1 : 20, 1 : 30, 1 : 50, and mixed with the aqueous solution of PVA at a ratio of 1 : 5.

Investigation of gel formation kinetics at positive temperatures was carried out by rheological measurements in the oscillatory mode with a HAAKE Viscotester iQ rheometer (Thermo Electron, Germany) at the frequency of 1 Hz using the measuring system of coaxial cylinders CC25; sample temperature was controlled with the Peltier element embedded into the rheometer. The principle of rheological measurements in the oscillatory mode is presented in [12], and the measurement procedure is described in the documentation to the rheometer and the software used.

To prepare cryogels, the formed gels were frozen at a temperature of –20 °C for 20 h, and then thawed for 4 h at a temperature of 20 °C.

To study sample deformation (γ) at a constant load with time, according to Kelvin–Voigt model, the upgraded Höppler viscometer designed at IPC SB RAS was used [13–15].

RESULTS AND DISCUSSION

For the primary characterisation of the compositions under investigation, the linear viscoelasticity (LVE) range of the formed gel was determined from the amplitude sweep shown in Fig. 1, *a*. The presented dependences were recorded for gel sample formed at 23 °C from the solution of 5 wt% PVA in distilled water and the composition IPC-PRO, diluted at a ratio of 1 : 20 with distilled water (5 % PVA – IPC-PRO (1 : 20)). Elastic modulus (G', Pa) and the loss modulus (G'', Pa), which are the components of the complex modulus, recorded in the oscillatory mode at the frequency of 1 Hz, are plotted on the vertical axis, while deformation (a dimensionless value) is plotted on the horizontal axis.

The linear viscoelasticity range was determined from the presented dependences (see Fig. 1, *a*, *b*): this is the region where G' and G'' curves go parallel to the horizontal axis, and the corresponding deformation values are ranging from 0.01 to 0.35. For other crosslinker concentrations, the LVE range also falls within the indicated interval. Subsequent kinetic experiments were carried out at the deformation value equal to 0.1.

The time dependences of elasticity modulus G', loss modulus G'', and complex viscosity modulus ($|\eta^*|$) depict the kinetics of structure forming process and provide an adequate characterisation of the formed structure because the mode of sample deformation based on the oscillatory motion of a test body does not destroy the forming gel. The recorded rheological dependences depict the physical process of liquid transformation into a nonflowable solid-like body. The kinetic dependences of G', G'' and $|\eta^*|$, recorded in the oscillatory mode at the deformation equal to 0.1 and frequency 1 Hz for the gel composed of 5 % PVA – IPC-PRO (1 : 20) are shown in Fig. 2. One can see that the dependences of G', G'' and $|\eta^*|$ demonstrate a rapid growth at the initial regions: gel formation starts immediately after component mixing. We see that $G' > G''$, which means that the elastic properties of the sample are prevailing. Then, in time, the rate of G', G'' and $|\eta^*|$ increase starts to decelerate, the curves reach almost horizontal region: a three-dimensional structure (gel) is formed in the whole volume of the sample. The initial section of the mentioned region can be considered as the time of gel formation within the whole volume, which is less than 1000 s on the presented scale. Then the values under consideration continue to increase substantially slower: the formed gel strengthens insignificantly. For the system type under consideration, G', G'' and $|\eta^*|$ change in phase with time, so further consideration will be limited to the kinetics of elastic modulus G', the parameter characterising the gel-like state of the substance.

The kinetic dependences of elastic modulus G', obtained at 10 and 23 °C for gel-forming systems with different crosslinker concentrations, show that with temperature decrease to 10 °C the sample in which the IPC-PRO composition is diluted 1 : 50 forms a gel with elastic modulus comparable with that of the composition for the gel in which IPC-PRO is diluted 1 : 30 at 23 °C (290 and 360 Pa, respectively). It should be noted that a substantial increase in G' to 600 Pa is recorded at a decreased temperature and (1 : 30) dilution of IPC-PRO composition. The time of gel formation within the whole cell volume, determined as the start of the quasi-linear region on the curves, is 100 s for the sample 5 % PVA – IPC-PRO (1 : 20)

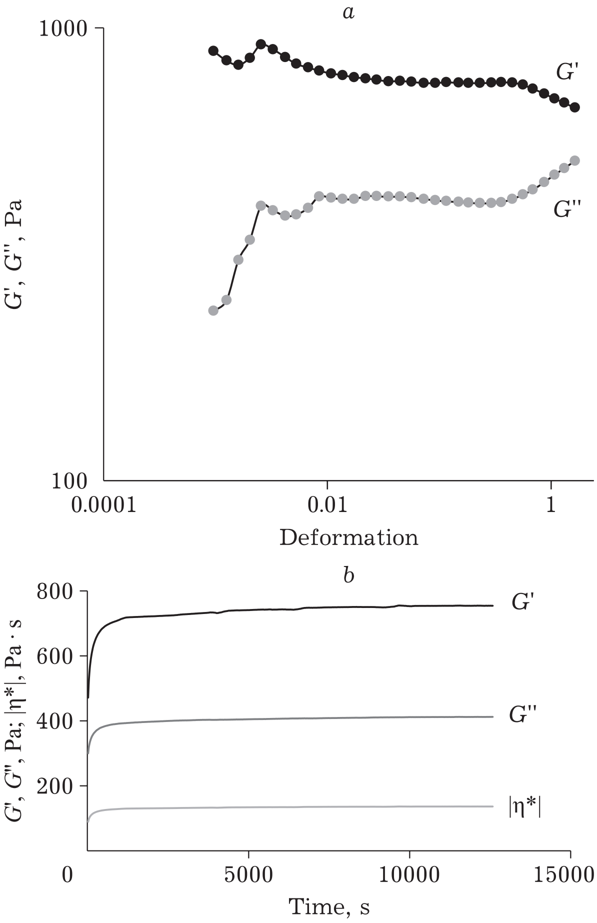

Fig. 1. Rheological characteristics (G', G'', $|\eta^*|$) of the gel based on 5 wt% PVA and the composition IPC-PRO/H_2O (1 : 20) at 23 °C in the controlled deformation mode (*a*) and the kinetic dependence of these parameters (*b*). Here and in Fig. 2: G' is elastic modulus, G'' is loss modulus, $|\eta^*|$ is the complex viscosity modulus.

and 150 s for the sample 5 % PVA – IPC-PRO (1 : 30). The value of modulus G' at these points is equal to 720 and 360 Pa, respectively, both compositions form a strong gel over the whole volume. In the case of the lowest crosslinker concentration in solution 5 % PVA – IPC-PRO (1 : 50) at 23 °C, gel is not formed within the whole sample volume, and for this case G' is equal to 120 Pa at the moment when the curve reaches its plateau. The discussed numerical values of G' are presented in Table 1. With an increase in crosslinker concentration in the system, the strength of the formed structure increases, while the time of gel formation decreases.

The dependences of elastic modulus G′ and the loss modulus G″ on temperature have been studied (see Fig. 2, *b*) under the conditions: the solution of 5 wt% PVA, dilution of the IPC-PRO composition 1 : 30, heating from 10 to 23 °C for

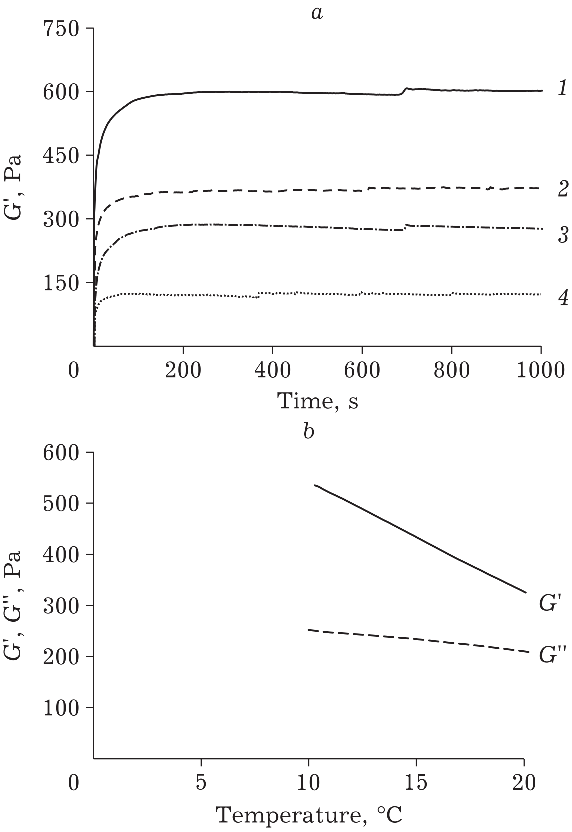

Fig. 2. Rheological characteristics of the gel based on 5 wt% PVA and the composition IPC-PRO: *a* – kinetic dependences of *G*′, recorded in the oscillatory mode for deformation equal to 0.1 and the ratio IPC-PRO/H_2O equal to 1 : 30 at 10 °C (*1*), 1 : 30 at 23 °C (*2*); 1 : 50 at 10 °C (*3*); 1 : 50 at 23 °C (*4*); *b* – temperature dependences of *G*′ and *G*″ at heating the gel from 10 to 23 °C for 2 min, at the ratio IPC-PRO/H_2O = 1 : 30. For designations, see Fig. 1.

2 min. One can see that the recorded dependences are linear, and the loss modulus G″ decreases slower with an increase in temperature than the elastic modulus G′ does. Within the experiment time (2 min), G′ decreases from 535 to 325 Pa, and G″ from 250 to 220 Pa. Extrapolation of the straight lines under consideration to higher temperatures gives the point at which G′ = G″, corresponding to the complete destruction of the structure.

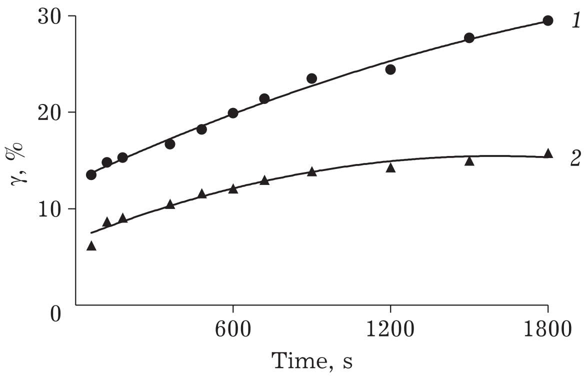

Fig. 3. Dependence of deformation (γ) on time for the samples of gel (*1*) and cryogel (*2*) prepared from 5 wt% PVA and the composition IPC-PRO/H_2O (1 : 20) at the constant strain of 7 kPa.

The dependence of deformation – compression on time for gel and cryogel, characterising the ability of materials to be deformed under mechanical strain, is presented in Fig. 3.

One can see that under constant load the larger deformation is exhibited by the gel (see Fig. 3, curve *1*), the value of γ reaches 25 % within experiment time (30 min). For the cryogel sample (see Fig. 3, curve *2*), the value of γ at the same strain is equal to 15 %. In the cryogel obtained after the cycle of freezing-thawing of the composition formed as a result of the chemical interaction of PVA macromolecules with IPC-PRO composition, in addition to chemical crosslinking, intermolecular interaction also occurs, which is accompanied by an increase in elastic properties.

Coal sample is a solid, dense black-coloured rock with a matte surface. After the deposition of IPC-PRO (1 : 20) composition on the coal surface, followed by treatment with the aqueous solution of 5 wt% PVA, the gel is formed within 20 min as a result of crosslinking. The image of the coal sample is shown in Fig. 4: immediately after treatment (*a*) and after drying (*b*). Coal surface after its treatment with the composition becomes tacky and glossy. Gel adhesion to the coal surface is observed, and after drying, a matte strong and water-resistance film is formed.

TABLE 1

Characteristics of the studied gel-forming systems

Formulation of the composition	Gel formation time, s		*G*′, Pa	
	23 °C	10 °C	23 °C	10 °C
5 % PVA – IPC-PRO (1 : 20)	100	–	720	–
5 % PVA – IPC-PRO (1 : 30)	150	200	360	600
5 % PVA – IPC-PRO (1 : 50)	–	220	120	290

Notes. 1. *G*′ – dynamic elastic modulus at the gel formation point. 2. Dash – not determined.

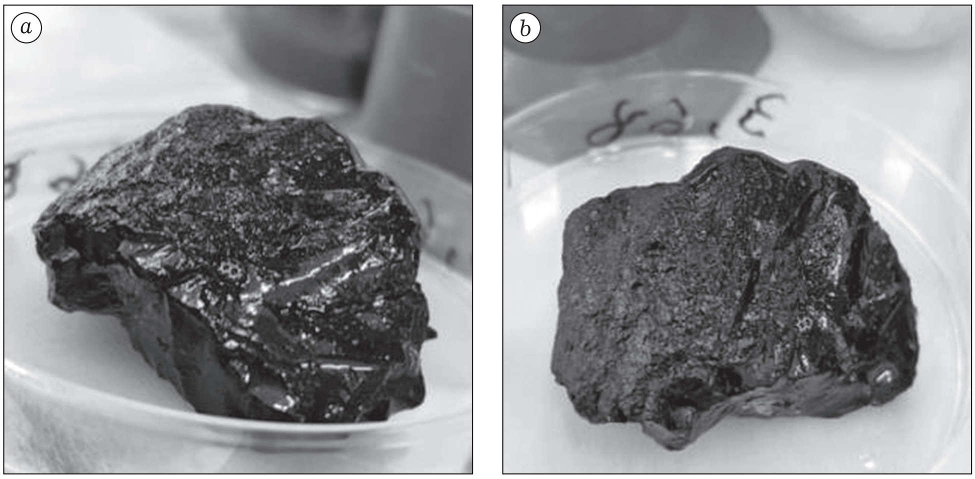

Fig. 4. Photographs of coal sample treated with the gel-forming composition: *a* – after deposition; *b* – after drying.

CONCLUSION

The features of the rheological behaviour of gel-forming systems based on PVA solution and IPC-PRO composition, promising from the viewpoint of coal surface protection from the access of oxygen, have been investigated. It has been determined from the recorded rheological dependences that the gel starts its formation at the moment of component mixing in the rheometer cell, and the time of gel formation within the whole volume can be determined as a point in which the dependence of the dynamic elastic modulus reaches its plateau. The relationship between elastic modulus and the loss modulus at which $G' > G''$ points to the prevalence of elastic properties in the gel during its formation, because the strength of the formed structure is characterised by G' value. With an increase in crosslinker concentration in the system (with decreased dilution of IPC-PRO composition), the strength of the formed structure increases, and the time of gel formation decreases. With a decrease in temperature, the strength of the gel increases. It has been determined that the gel gets additionally stabilised after the freezing-thawing cycle: cryogel sample tested under static conditions is deformed less than the corresponding gel under the same load.

The developed formulation of the composition possesses strength properties and good adhesion to coal surface, it can be used to protect coal from self-ignition in open-pit mines, to simplify the formation of cracks and disintegration of coal seams during the interval hydraulic fracturing, and as a protection from coal dust at the technological roads of coal mining enterprises.

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