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Cryogels based on gel-forming compositions and polymer mixtures

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Abstract

An integrated method of mining quarry reclamation and landscaping is presented. The essence of the method is in making a protective layer of gel-forming composition, based on polyvinyl alcohol (PVA) and IKhN-PRO composition, including borax, on the surface of solid toxic rock. A fertile ground containing plant seeds is applied onto the surface of the protective layer; its surface is treated with a solution of PVA mixture and carboxymethylated starch (CMS). After the freezing-thawing cycle, soil-structuring cryogel is formed, which retains moisture, heat and makes comfortable conditions for plants. The rheological properties of the gel-forming composition were investigated; the time of gel formation at a temperature of 20 and 10 °C was determined to be 200 and 150 seconds, respectively. The rheological characteristics of the solutions of PVA and CMS mixture were studied. It is shown that with an increase in the polymer concentration in the mixture the viscosity increases. Dry films obtained on the basis of a mixture of PVA, CMS and cryogels swell in water. Phytotoxicity of the method was studied for coal samples. The biometric data of plants have shown that the productivity of plant biocenosis in experimental samples is much higher than in control samples.

Keywords: polyvinyl alcohol, cryogel, gelation, viscosity, elastic modulus, coal, reclamation

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INTRODUCTION

Coal mining has a significant impact on the environment, leading to its large-scale transformation. Mining quarries surrounded by overburden dumps require reclamation and restoration of vegetation layer. The most widespread reclamation technology involves applying a layer of fertile soil to the levelled surface of coal waste and forming technosols [1, 2].

Despite the measures taken, it has not been possible to eliminate the anthropogenic impact and restore the original landscapes. A geochemical anomaly has been observed in the soils on the surface of the coal mines, which has a negative impact on plant growth. Reclamation and restoration of vegetation in coal mines remains a pressing issue, for which an integrated method can be proposed. The essence of the method is in creating an insulating hydrogel on the surface of man-made eluvium to prevent the migration of harmful substances into the fertile soil layer and in covering it with a biodegradable cryogel to protect seeds from weathering. It is known that hydrogels based on polyvinyl alcohol (PVA) cross-linked with borax are used as a barrier material for covering chemicals [3]. Cryogels are obtained from an aqueous solution of synthetic polymer (PVA) or natural starch [4–6]. By combining the properties of synthetic polymer (strength) and natural material (biodegradation), it is possible to obtain a composite material that will structure the soil, retain heat and moisture, creating comfortable conditions for seed germination, and then undergo biodegradation [7].

The aim of this work is to study the rheological and physicochemical properties of a gel-forming composition (hydrogel), solutions of a mixture of PVA and starch, as well as their cryogels.

EXPERIMENTAL

To prepare an aqueous solution of PVA (molecular mass $M \sim 60 \cdot 10^3$), the polymer powder was added in small portions to hot water (80 °C) with stirring and dissolved for 2–4 h. The gel-forming composition (hydrogel) is formed as a result of intermolecular interaction between the aqueous solution of PVA (gelling agent) and the aqueous solution of the alkaline composition IKhN-PRO (cross-linking agent) based on an inorganic buffer system and polyol, which contains borax [8]. In this work, the IKhN-PRO composition was diluted with distilled water in a ratio of 1 : 30.

To obtain a hydrogel, a 5 % aqueous solution of PVA was stirred and small portions of the IKhN-PRO composition were added in a ratio of PVA / IKhN-PRO = 5 : 1 (by mass).

Rheological characteristics were measured in oscillation mode on a HAAKE Viscotester iQ rheometer (Thermo Electron, Germany) at a frequency of 1 Hz using a CC25 coaxial cylinder measuring system at temperatures of 10 and 20 °C. The method has a measurement error of ±5 % [9].

To obtain a biodegradable PVA-based cryogel, carboxymethylated starch (CMS) (Policell LLC, Russia), which dissolves in cold water, was used as a natural polymer. To prepare the mixture, CMS powder was added to an aqueous PVA solution and stirred for 1 h. The compositions of the analysed aqueous solutions are presented in Table 1. Each composition was studied in three variants, and the results are presented as average values. Cryogels based on a mixture of PVA + CMS were obtained after one freezing-thawing cycle. Freezing was carried out at a temperature of −20 °C for 20 h, and thawing was carried out at a temperature of 20 °C for 4 h. Under similar conditions, a freezing-thawing cycle was performed on the hydrogel.

The change in mass of hydrogel and cryogel samples during storage in water was assessed using a gravimetric method. To do this, the sample was placed in a beaker with distilled water for 24 h at a temperature of 20 °C, then removed from the water, excess liquid was carefully removed from its surface with filter paper, and then the sample was weighed and placed back in water.

The elastic modulus of cryogels was determined using a laboratory setup based on Maxwell's rheological model. The cryogel sample was subjected to compression deformation (γ) and the elastic stress (σ) was determined. The instantaneous elastic modulus (E, kPa) was calculated using Hooke's law ($E = \sigma/\gamma$) [10, 11].

To simulate the reclamation process, coal was placed in a container with an area of 0.02 m^2, onto which a composition of IKhN-PRO (0.2 L/m^2) was sprayed as a cross-linking agent, followed by a 5 % aqueous solution of PVA (0.4 L/m^2) as a gelling agent. As a result of cross-linking, a hydrogel formed on the surface of the coal. Next, the containers with samples were subjected to one freezing-thawing cycle. The treated coal was covered with a 0.4 m layer of soil and sown with 2 g of grass mixture seeds, then a solution of PVA + CMS mixture was applied to the surface at a rate of 3.5 L/m^2 (70 mL per container). The control sample was treated with the corresponding volume of distilled water. The containers with coal and soil were frozen at a temperature of −6 °C, then thawed and incubated at room temperature (20 °C) and constant humidity. To assess phytoproductivity, 20 days after the start of the experiment, the above-ground mass was completely cut off, dried at 85 °C and weighed. Based

TABLE 1

Composition of the analysed aqueous solutions and corresponding cryogels

Sample	Component content, mass %		
	PVA	CMS	Water
1	0	1.0	99.0
2	0	2.0	98.0
3	0	3.0	97.0
4	3	2.0	95.0
5	4	2.0	94.0
6	5	0	95.0
7	5	0.5	94.5
8	5	1.0	94.0
9	5	2.0	93.0

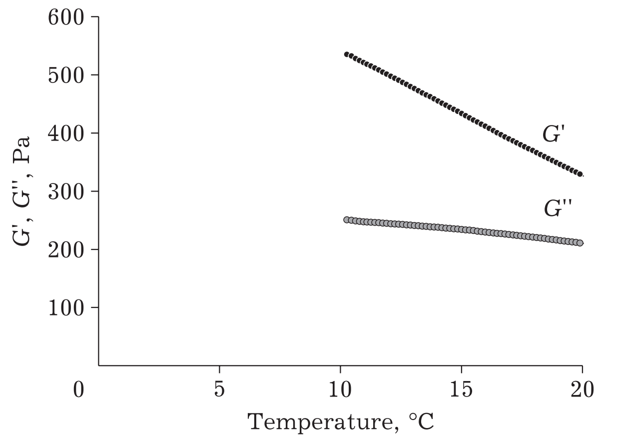

Fig. 1. Dependence of the elastic modulus (G') and loss modulus (G'') on the heating temperature of a hydrogel based on 5 % PVA + IKhN-PRO. Heating time from 10 to 20 °C – 2 min.

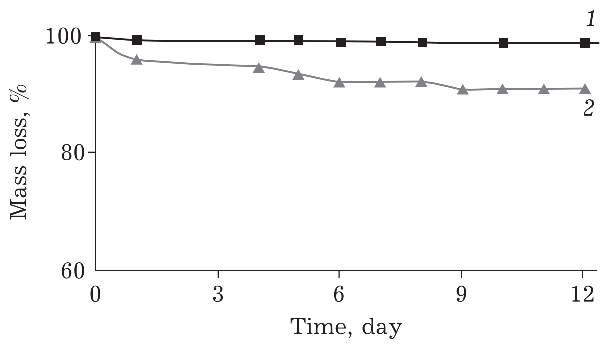

Fig. 2. Mass loss of hydrogel samples based on 5 % PVA + + IKhN-PRO relative to the initial mass when stored in water: *1* – after a freezing-thawing cycle; *2* – without freezing.

on the data obtained, the productivity of the plant biocenosis per m^2 was calculated [12].

The experiment was conducted in the following variants:

– Experiment 1. Coal was covered with soil containing seeds (control).

– Experiment 2. Coal was covered with hydrogel, then soil containing plant seeds was applied, on the surface of which cryogel based on a 5 % aqueous solution of PVA was applied.

– Experiment 3. Coal was covered with hydrogel, then soil containing plant seeds was applied, on the surface of which cryogel based on a 1 % aqueous solution of CMS was applied.

– Experiment 4. Coal was covered with hydrogel, then soil containing plant seeds was applied, on the surface of which cryogel based on a solution of a mixture of 5 % PVA + 1 % CMS was applied.

– Experiment 5. Coal was covered with hydrogel, then soil containing plant seeds was applied, on the surface of which cryogel based on a solution of a mixture of 2.5 % PVA + 1 % CMS was applied.

In experiments 2–5, coal samples covered with hydrogel were subjected to a freezing-thawing cycle.

RESULTS AND DISCUSSION

The rheological dependencies of the elastic modulus (G'), loss modulus (G'') and complex viscosity modulus ($|\eta^*|$) reflect the kinetics of the process of transforming a liquid into a non-flowing solid-like body (gel) [13]. When mixing the PVA solution and the IKhN-PRO composition, the gel formation process begins at the initial stage, which is reflected in a sharp increase in the values of G' and G'', i.e., the elastic properties $G' > G''$ prevail. Then, over time, the rates of increase of G', G'' and $|\eta^*|$ decrease, the curves reach a practically horizontal section – a three-dimensional structure (gel) is formed throughout the entire volume of the sample. The gelation time throughout the entire volume of the cell is determined as the beginning of the quasi-linear section of the curves.

The dependence of the elastic modulus G' and loss modulus G'' on temperature is linear (Fig. 1). The loss modulus G'' decreases slower with increasing temperature than the elastic modulus G'. During the experiment (2 min), G' decreases from 535 to 325 Pa, and G'' decreases from 250 to 220 Pa. Extrapolation of the considered straight

TABLE 2

Characteristics of gelation

Composition of the mixture	Gel formation time, s		Value of dynamic elastic modulus (G') at the point of gelation, Pa	
	20 °C	10 °C	20 °C	10 °C
5 % PVA + IKhN-PRO (ratio 5 : 1)	150	200	360	600

lines to the region of higher temperatures gives a point at which $G' = G''$. This point corresponds to complete destruction of the structure (Table 2). The mass of the hydrogel based on 5 % PVA + IKhN-PRO after one freezing-thawing cycle when stored in water for 10 days remains practically unchanged (Fig. 2). The mass of the hydrogel without a freezing-thawing cycle when the sample is stored in water decreases by no more than 10 %.

To obtain cryogels, it is necessary to select the composition of the PVA + CMS mixture solution, which will be homogeneous for at least 24 hours.

Rheological studies of aqueous solutions of CMS and solutions of a mixture of PVA + CMS (Fig. 3) showed that as the concentration of polymers in the mixture solution increases, the viscosity increases (see Fig. 3, *a*, *b*). The viscosity of a 1 % CMS solution does not change within 2 days. The viscosity of a 2 % CMS solution decreases by no more than 2 % over 2 days (within the margin of error of the method). It is noted that the viscosity of a 3 % CMS solution decreases by 13.4 % after 2 days and by 26 % after 13 days. This may be due to the degree of substitution of hydroxyl groups with carboxymethyl groups, which affects the solubility of starch in water and, consequently, the stability of solutions. In solutions of a mixture of PVA + 2 % CMS, the viscosity increases with an increase in the concentration of PVA (see Fig. 3, *b*). During storage of the mixture solutions, cloudiness is observed due to the formation of aggregates, the sedimentation of which leads to a decrease in viscosity.

It is noted that the rheological behaviour of polymer mixture solutions affects the properties of cryogels. As the concentration of CMS in the mixture increases, the viscosity of the solution and the elastic modulus of the cryogels increase (see Fig. 3, *c* and *d*, respectively). The viscosity of a solution of 5 % PVA + 1 % CMS mixtures does not change within 24 h and is 72 mPa · s, which allows for effective spraying with mechanised tools and equipment, while the elastic modulus of this mixture solution is 13.4 kPa.

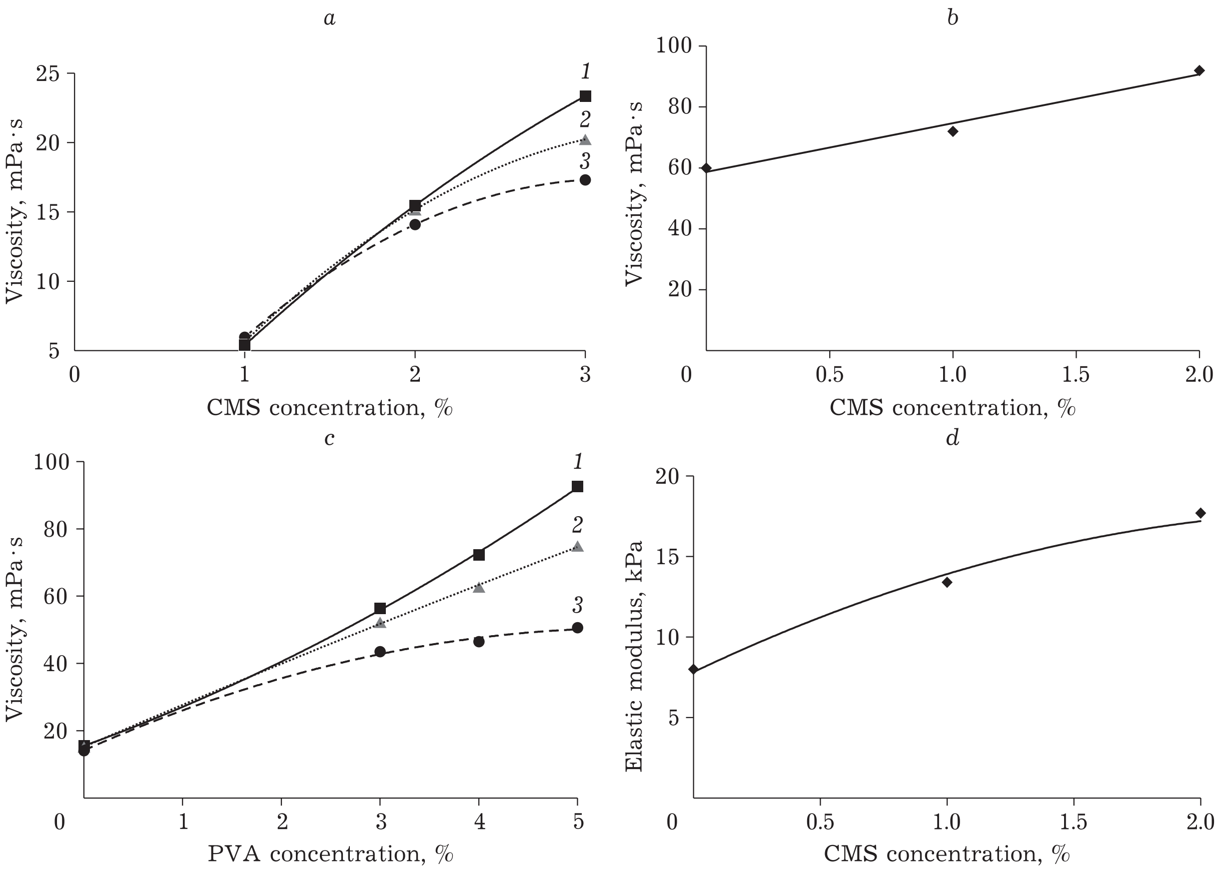

Fig. 3. Rheological characteristics of solutions and cryogels: viscosity of CMS solution (*a*) and solution of PVA + 2 % CMS mixture (*b*) after 1 (*1*), 3 (*2*) and 14 days (*3*); viscosity of solution of 5 % PVA + CMS mixture after 1 day (*c*); elastic modulus of cryogels based on a solution of a mixture of 5 % PVA + CMS (*d*).

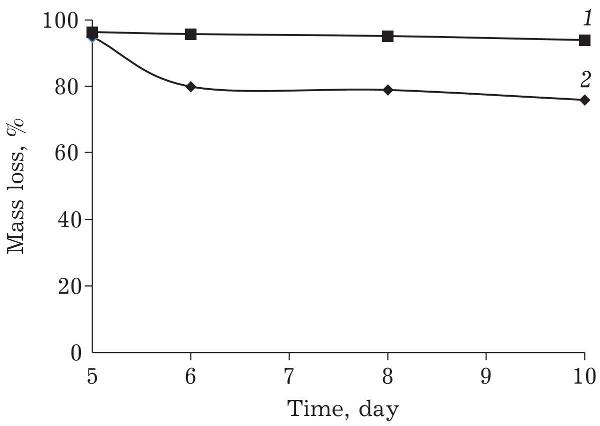

Fig. 4 Mass loss of swollen films obtained from a solution of a mixture of 5 % PVA + 1 % CMS: cryogel (*1*); solution (*2*).

TABLE 3

Plant phytoprodutivity when using cryogel

Experiment number*	Seed germination rate, %	Productivity of the biocenosis, g/m^2
1	98	49
2	95	206
3	96	362
4	96	406
5	97	400

* The experiment number corresponds to the data in Fig. 5.

For practical application, it is necessary to consider the physicochemical properties of films obtained from the mixture solution and cryogel (Fig. 4), since the formation of cryogel depends on weather conditions.

Initially, when the films came into contact with water, an increase in mass was observed. After 5 days, the degree of swelling of the film obtained from the solution mixture was 452 %, which is almost half that of the cryogel film (890 %). Then the mass of the swollen films decreased. The mass loss of the cryogel-based film was no more than 5 %, and that of the solution-based film was 25 %. The mass loss of the swollen sample obtained from the mixture solution (without freezing) is due to the presence of only hydrogen bonds between the polymer chains, as a result of which the structure of the sample is destroyed in water.

Modelling of an integrated method of reclamation showed that despite the high germination rate of seeds in the control experiment, the productivity of the biocenosis is low (Fig. 5, Table 3). As a result of watering, geochemical changes

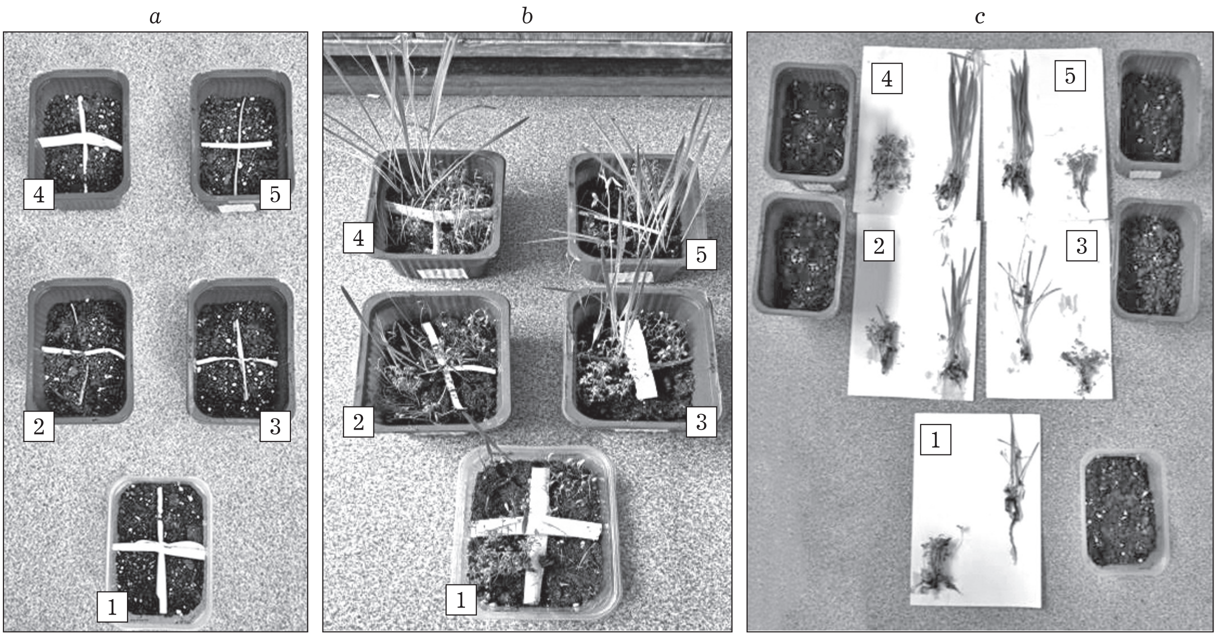

Fig. 5. Plant growth in different variants: *a* – experiment started; *b* – plants in soil after 14 days; *c* – plants removed from soil after 14 days. Conditions of experiments 1–5 correspond to: *1* – coal covered with soil containing seeds (control); *2* – coal covered with hydrogel, soil with seeds, cryogel based on an aqueous solution of 5 % PVA; *3* – coal covered with hydrogel, soil with seeds, cryogel based on an aqueous solution of 1 % CMS; *4* – coal covered with hydrogel, soil with seeds, cryogel based on a solution of 5 % PVA + 1 % CMS; *5* – coal covered with hydrogel, soil with seeds, cryogel based on a solution of 2.5 % PVA + 1 % CMS.

occur in the soil, leading to uncomfortable conditions for plant growth. The greatest increase in biomass (approximately 8 times) relative to the control (experiment 1) was observed in experiments 4 and 5. The mixture solutions form elastic cryogels that retain moisture and heat, which is important for plant growth, and the CMS also serves as a nutrient environment.

CONCLUSION

When the PVA solution reacts chemically with the IKhN-PRO composition, a hydrogel is instantly formed, and its water resistance increases after a freezing-thawing cycle. The hydrogel protects the soil from the migration of harmful substances, which is confirmed by the phytoproductivity of plants. A solution of PVA + CMS mixture applied to the soil surface forms a cryogel after a freezing-thawing cycle, which stabilises the soil and creates optimal conditions for plant growth. The proposed integrated method of reclamation and landscaping of man-made objects, tested on coal samples, demonstrates its effectiveness.

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