

FUEL AND ENERGY COMPLEX OF UKRAINE AND TRENDS IN THE USE OF MINERAL FUELS

DOI <https://doi.org/10.30525/978-9934-26-219-7-8>

DESIGN AND STUDY OF HYDROGELS AND BIOPOLYMERS MODIFIED BY HUMIC ACIDS

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INTRODUCTION

Modern using the environmentally friendly biodegradable polymeric materials, which implement the principle of “zero waste” throughout the life cycle – “production-use-disposal” – is global trends now¹. According to the production method, environmentally friendly biodegradable polymeric materials can be^{2, 3}:

- polymers that are directly derived from plant or animal biomass (polysaccharides, proteins, lipids, etc.),
- polymers obtained by classical chemical synthesis from renewable monomers on a biological basis, such as polylactic acid (PLA),
- polymers obtained by natural or genetically modified microorganisms, such as polyhydroxyalkanoates (PHAs), polyhydroxybutyrates (PHBs), bacterial cellulose, xanthan, gelatin, pullulan and others.

Using such a large range of environmentally friendly biodegradable polymer matrices allows to produce polymer materials with sufficient gas insulation and heat resistance, which can be processed into different products and parts for various industries⁴.

¹ W. Stahel, “The circular economy” *Nature* 531. Pp. 435–438 (2016). DOI: <https://doi.org/10.1038/531435a>

² G. Kaur, K. Uisan, K. Lun Ong, C. Ki Lin, “Recent Trends in Green and Sustainable Chemistry & Waste Valorisation: Rethinking Plastics in a circular economy” *Curr. Opin. Green Sustain. Chem.* 9, pp. 30–39 (2018). DOI: <https://doi.org/10.1016/j.cogsc.2017.11.003>

³ C. Cecchini, “Bioplastics made from upcycled food waste. Prospects for their use in the field of design” *The Design Journal* 20, pp. 1596–1610 (2017). DOI: <https://doi.org/10.1080/14606925.2017.1352684>

⁴ S. Bessada, R. Alves, M. Oliveira, “Coffee Silverskin: A Review on Potential Cosmetic Applications” *Cosmetics* 5, pp. 5 (2018). DOI: <https://doi.org/10.3390/cosmetics5010005>

That is why in different industries world trend is environmentally friendly polymeric materials and compositions using that do not have negative environmental impact and have better operational and aesthetic advantages over other materials. These include properties such as high strength and durability, light weight and wide possibilities in design, color scheme and other important aesthetic characteristics. A characteristic producing feature for structures and products from environmentally friendly polymeric materials production is the optimizing their component composition and performance characteristics set task. In fact, almost always the high quality and durability of polymer products and structures is due to aet of correct material choice and the most effective processing method selection.

At the same time, the characteristics level of impact strength, heat resistance, gas permeability and antisepticity for environmentally friendly biodegradable polymeric materials often do not meet the application conditions requirements⁵. That is why it iserspective to keep hybrid environmentally friendly biodegradable polymeric materials modified with inorganic and organic nature reagents.

Today, hybrid polymer-inorganic nanocomposites are used to produce materials with semiconductor and superconducting properties, and hybrid polymers modification allows to produce composites with high fire resistance^{6,7}. Most frequently, as hybrid polymers modifiers, layered natural or synthetic silicates montmorillonite, gallosite, silica, laponite, etc. are used. Also, as shown in publications⁸, the silicates inclusion in biopolymers film has a number of advantages due to their low cost, availability and good surface quality. At the same time, along with the advantages of hybrid polymers modification with silicate substances, there are some problematic aspects related to the potential modifications toxicity that should be considered when migrating from environmentally friendly biodegradable

⁵ F. C. Cabrera, “Eco-friendly polymer composites: A review of suitable methods for waste management” *Polymer Composites* 42, pp. 2653– 2677 (2021). DOI: <https://doi.org/10.1002/pc.26033>

⁶ L. Pinto, M. Bonifacio, De G. E. Addolorata, E. Santovito, S. Cometa, A. Bevilacqua, F. Baruzzi, “Biopolymer hybrid materials: Development, characterization, and food packaging applications” *Food packaging and shelf life* 28, 100676 (2021). DOI: <https://doi.org/10.1016/j.fpsl.2021.100676>

⁷ J. Pires, C. D. D. Paula, V. G. L. Souza, A. L. Fernando, I. Coelho, “Understanding the barrier and mechanical behaviour of different nanofillers in chitosan films for food packaging” *Polymers* 13(5), pp. 721 (2021). DOI: 10.3390/polym13050721

⁸ J. R. A. Pires, V. G. L. Souza, A. L. Fernando, “Chitosan/montmorillonite bionanocomposites incorporated with rosemary and ginger essential oil as packaging for fresh poultry meat” *Food Packaging and Shelf Life* 17, pp.142–149 (2018). DOI: <https://doi.org/10.1016/j.fpsl.2018.06.011>

polymeric materials for packaging and food packaging. No less important type of hybrid polymeric materials are their modifications using different carbon substances: graphene, graphene oxide, carbon nanotubes, fullerenes and others⁹.

Low-metamorphic coal (brown coal, partially flame coal) and its derivatives can be an effective and perspective antibacterial modifier and composite filler, as coal is resistant to water and many chemicals and is characterized by fungal and microbial resistance. Also, such coal contains many different functional groups that determine the possibility of interaction with different types of polymer matrices.

Today, there is a lot of research on the use of coal materials, derivatives and waste as fillers for polymeric and composite materials^{10, 11, 12, 13, 14}. One of the most likely sources of modifiers and fillers for polymers may be humic acids, which are usually obtained from brown coal¹⁵. Currently, brown coal has very limited use due to poor technological characteristics (high content of ash, moisture and sulfur) and therefore cannot be used for combustion in thermal power plants. To create the possibility of using this type of combustible minerals, it is proposed to use brown coal in the process

⁹ S. Sharma, B. P. Singh, "Mechanical Properties of Graphene–Carbon Nanotube Reinforced Hybrid Polymer Nanocomposites" *All-carbon Composites and Hybrids* 12, pp. 278–316 (2021). DOI: <https://doi.org/10.1039/9781839162718-00278>

¹⁰ G. Gong, B.-H. Xie, M.-B. Yang, W. Yang, W.-Q. Zhang, and M. Zhao, "Mechanical properties and fracture behavior of injection and compression molded polypropylene/coal gangue powder composites with and without a polymeric coupling agent," *Compos. Part Appl. Sci. Manuf.*, vol. 38, no. 7, pp. 1683–1693, Jul. 2007. DOI: [10.1016/j.compositesa.2007.02.002](https://doi.org/10.1016/j.compositesa.2007.02.002)

¹¹ U. Atikler, D. Basalp, and F. Tihminlioglu, "Mechanical and morphological properties of recycled high-density polyethylene, filled with calcium carbonate and fly ash," *J. Appl. Polym. Sci.*, vol. 102, no. 5, pp. 4460–4467, Dec. 2006. DOI: <https://doi.org/10.1002/app.24772>

¹² I. Ahmad and P. A. Mahanwar, "Mechanical properties of fly ash filled high density polyethylene," *J. Miner. Mater. Charact. Eng.*, vol. 9, no. 3, pp. 183–198, 2010. URL: <https://www.scirp.org/html/20719.html>

¹³ S. G. Pardo, C. Bernal, A. Ares, M. J. Abad, and J. Cano, "Rheological, thermal, and mechanical characterization of fly ash-thermoplastic composites with different coupling agents," *Polym. Compos.*, vol. 31, no. 10, pp. 1722–1730, Oct. 2010. DOI: <https://doi.org/10.1002/pc.20962>

¹⁴ H. Potgieter, C. LIAUW, and D. Velado, "Properties and performance of simulated consumer polymer waste-coal combustion byproduct composite material," *Polym. Eng. Sci.*, vol. 54, no. 6, pp. 1239–1247, May 2014. DOI: [10.1002/pen.23668](https://doi.org/10.1002/pen.23668)

¹⁵ Yagovkin A. K., Mironova Yu.V., Mironov A. V. Development of ideas about the molecular organization of complex organic systems of humic acids. *Bulletin of Ugra State University*. 2009. Vol. 3 (3). P. 80–60.

of oxidative desulfurization^{16, 17}, for the production of components of boiler fuel or bitumen^{18, 19} and in the processes of its gasification²⁰. However, the most promising is the use of brown coal for the production of humic substances and acids and the subsequent production of polymers and various types of materials based on them. Previous works^{21, 22, 23, 24} show ways to obtain polymer hydrogels that are modified with humic substances. It has been shown that humic acids have a specific effect on the structure formation processes in gelatin-based polymer hydrogels due to the different nature and characteristics of humic substances: the degree of metamorphism

¹⁶ Gunka V., Pyshyev S. Lignite oxidative desulphurization. Notice 2: effects of process parameters. *International Journal of Coal Science and Technology*. 2015. 2. P. 196–201. DOI: 10.1007/s40789-015-0056-3

¹⁷ Pysh'yev S., Gunka V., Bratychak M., Grytsenko Yu. Kinetic regularities of high-sulphuric brown coal oxidative desulphurization. *Chemistry & Chemical Technology*. 2011. Vol. 5(1). P. 107–113. DOI: <https://doi.org/10.23939/chcht05.01.107>

¹⁸ Gunka V., Shved M., Prysiashnyi Y., Pyshyev S., Miroshnichenko D. Lignite oxidative desulphurization: notice 3 – process technological aspects and application of products. *International Journal of Coal Science & Technology* 2019. Vol. 6. P. 63–73. DOI: 10.1007/s40789-018-0228-z

¹⁹ Gunka V., Pyshyev S. Technology of oxidative desulphurization of lignite *Petroleum & Coal*. 2015. Vol. 57 (6). P. 696–704.

²⁰ Bielowicz B., Kasiński J. R. The possibility of underground gasification of lignite from Polish deposits. *International Journal of Coal Geology*. 2014. Vol. 131. P. 304–318. DOI: 10.1016/j.coal.2014.06.025

²¹ V. Lebedev, D. Miroshnichenko, Z. Xiaobin, S. Pyshyev, D. Savchenko, “Technological Properties of Polymers Obtained from Humic Acids of Ukrainian Lignite” *Petroleum and Coal* 63 (3), pp. 646–654 (2021).

²² Лебедєв В. В., Мірошніченко Д. В., Савченко Д. О., Мазченко М. В., Лендич Є. С., Борісенко Л. М. Вивчення особливостей отримання гелів на основі агар-агару для екології, косметології та медицини з антибактеріальними властивостями : *Сталий розвиток: захист навколишнього середовища. Енергоощадність. Збалансоване природокористування* : збірник матеріалів 6 Міжнародного молодіжного конгресу. Львів : Західно-Український Консалтинг Центр (ЗУКЦ), ТзОВ, 2021. 314 с. С. 269.

Лебедєв В. В., Мірошніченко Д. В., Савченко Д. О., Мазченко М. В., Лендич Є. С., Борісенко Л. М. Дослідження властивостей полімерних гідрогелів, модифікованих гуміновими кислотами. *Хімічні проблеми сьогодення (ХПС–2021)* : збірник тез доповідей IV Міжнародної (XIV Української) наукової конференції студентів, аспірантів і молодих учених, 23–25 березня 2021 р., м. Вінниця ; Донецький національний університет імені Василя Стуса ; редколегія: О. М. Шендрик (відп. ред.) та ін. Вінниця, 2021. 224 с.

²⁴ Lebedev V., Miroshnichenko D., Xiaobin Z., Pyshyev S., Savchenko D. Technological Properties of Polymers Obtained from Humic Acids of Ukrainian Lignite. *Сучасні технології переробки паливних копалин* : тези доповідей IV Міжнародної науково-технічної конференції, 15–16 квітня 2021 р. / укл. Мірошніченко Д. В. Харків : ТОВ «Планета-Прінт». 105 с.

of the source coal, volatile matters and oxygen content. It was also found that humic substances are active antibacterial agents of the hydrogel, which slow down the formation of mold in them²³. Modification of polymeric materials in the form of films and composites has also been studied^{25, 26}.

The purpose of this research is to study the features of the production processes and properties of polymer hydrogels based on gelatin, biofilms based on polyvinyl alcohol and hydroxypropylmethylcellulose modified with humic acids.

1. Determination of quality indicators of research raw materials

Humic acid was obtained according to GOST 9517-94²⁷. The essence of the method consists in processing an analytical fuel sample with an alkaline solution of sodium pyrophosphate, subsequent extraction of the sample with a solution of sodium hydroxide, precipitation of humic acids with an excess of mineral acid, and determination of the mass of the resulting sediment.

In total, three samples of humic acids were used, obtained from three samples of brown coal. The results of determining the quality of brown coal samples are shown in tables 1–4. It should be noted that the samples of coal differ slightly, namely: the content of analytical moisture ranges from 8.1 % to 30.6 %; ash content from 8.3 % to 48.7 %; total sulfur content from 1.87 % to 4.00 %; the volatile matters, calculated on the dry organic matter, from 47.7 % to 63.0 %. Indicators of ultimate analysis and yield of humic acids vary depending on the volatile matters.

Table 1

Proximate analysis of brown coal

Sample	Proximate analysis, %			
	W ^a	A ^d	S ^d _t (S ^{daf} _t)	V ^{daf} (V ^d)
1	16.8	48.7	2.08 (2.50)	56.7 (29.1)
2	8.1	8.3	1.72 (1.87)	47.7 (43.7)
3	30.6	36.7	2.78 (4.00)	63.0 (43.7)

²⁵ V. Lebedev, D. Miroshnichenko, Z. Xiaobin, S. Pyshyev, D. Savchenko. Use of Humic Acids from Low-Grade Metamorphism Coal for the Modification of Biofilms Based on Polyvinyl Alcohol. *Petroleum and Coal* 63(4), pp. 953–962 (2021).

²⁶ Чжан С., Мірошніченко Д. В., Лебедев В. В. Використання гумінових кислот для модифікації біодеградабельних плівок, виготовлених на основі полівінілового спирту та гідроксипропілметилцелюлози. *Вуглехімічний журнал*. № 6. 2021. С. 22–37.

²⁷ Solid fuel. Methods for determining the yield of humic acids, GOST 9517-94 (1996).

Table 2

Ultimate analysis of brown coal

Sample	Ultimate analysis, %				
	C ^{daf}	H ^{daf}	N ^{daf}	S ^{d_t}	O ^{daf_d}
1	80.83	4.48	1.29	2.50	10.9
2	68.10	4.57	1.35	1.87	24.11
3	60.71	4.87	1.30	4.00	29.12

Table 3

Total mass fraction and yield of free humic acids

Sample	(HA) ^{daf_t} , %	(HA) ^{daf_t} , %
1	87.60	79.44
2	49.66	44.27
3	82.94	75.30

Table 4

Chemical composition of brown coal ash

Sample	Chemical composition, %							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	SO ₃
1	70.08	9.83	3.24	0.88	5.43	0.77	0.90	5.90
2	No data							
3	No data							

To obtain polymers, we used food gelatin grade P-11 according to GOST 11293-89²⁸, the main quality indicators are given in table 5.

Table 5

Quality indicators of P-11 gelatin

№	Indicator name	Characteristics and norm
1	2	3
1	Appearance	Grains
2	Color	Light yellow
3	Smell	Absent
4	Taste	tasteless
5	Particle size, mm, no more	10
6	Mass fraction of particles less than 0.5 mm, %, no more	30

²⁸ Gelatin. Technical conditions, GOST 11293-89 (2001).

Completion of Table 5

7	Duration of dissolution, min, no more	25
8	The indicator of the activity of hydrogen ions in aqueous solution of gelatin with a mass fraction of 1 %, units, pH	from 5 to 7
9	Mass fraction of moisture, %, no more	16
10	Mass fraction of ash, %, no more	2.0
11	Strength of jelly with a mass fraction of gelatin 10 %, N, not less	11
12	Dynamic viscosity of solution with a mass fraction gelatin 10 %, mPa·s, not less	20.0
13	Melting point of jelly with mass fraction gelatin 10 %, °C, not less	32
14	The transparency of the solution with a mass fraction of gelatin 5 %, %, not less	45
15	Impurities, %, no more	Not allowed
16	Sulfurous acid in terms of SO ₂ , %, no more	0.075
17	Mesophilic aerobic and facultative anaerobic microorganisms, CFU, in 1 g of gelatin, no more	1·10 ⁵
18	Coliform bacteria (coliforms) in 0.01 g of gelatin	Not allowed
19	Pathogenic microorganisms, including salmonella, in 25 g	Not allowed
20	Gelatin-thinning bacteria, CFU, in 1 g of gelatin, no more	2·10 ²

We used polyvinyl alcohol (Kuraray, Japan) of the “Mowiol 6-98” (Clariant brand) with a degree of hydrolysis of 98.4 %, a solid content of 98.9 %, and a molecular weight (Mw) of 150,000. Hydroxypropylmethylcellulose brand Walocel™ manufactured by Dow Corning (USA) was also used in the research. Hydroxypropylmethylcellulose (Fig. 1) is a natural polymer that dissolves easily and quickly in hot or cold water, forming solutions with different viscosity levels. The main physical properties of hydroxypropylmethylcellulose are shown in table 6.

Citric acid (99.88 %) according to GOST 3652²⁹ is used as a catalyst for crosslinking of hybrid environmentally friendly biodegradable polymer films.

²⁹ GOST 3652-69. Reagent. Citric acid, monohydrate and anhydrous. *Specifications*. URL: <https://docs.cntd.ru/document/1200017479>

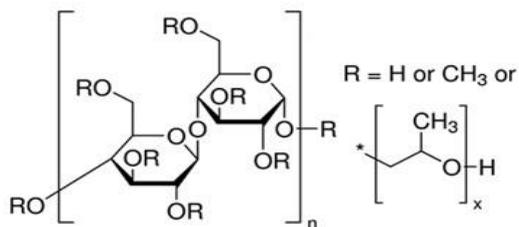


Fig. 1. Structural formula of hydroxypropylmethylcellulose

Table 6

Physico-chemical properties of hydroxypropylmethylcellulose

Indicator	Value
Solubility	water-soluble, delayed solubility in cold water with neutral pH
Moisture capacity	7.0 %
Color	White
pH 1 % solution	6.4

2. Experimental techniques and methodology

Hydrogels from gelatin and humic acids were prepared as follows. First, a 10 % gelatin solution was made in distilled water at a temperature of 90–100 °C. After that, by mixing, solutions with humic acids were obtained, in which the concentration of the latter was 0, 5, 10 and 15 %.

Solutions of polyvinyl alcohol with a concentration of 10 % obtained by dissolving the polymer in a ratio of 1:10 polyvinyl alcohol: distilled water when heated to 90–100 °C. To analyze the rheological properties, solutions of polyvinyl alcohol were obtained at various concentrations of humic acid (5, 10, 15 % wt.). The samples were stirred at room temperature until the polyvinyl alcohol was completely dissolved.

Solutions of hydroxypropylmethylcellulose at a concentration of 2 % of the mass were obtained by dissolving the polymer in a ratio of 2:100 hydroxypropylmethylcellulose:distilled water when heated to 90–100 °C. Then added to the obtained solutions of hydroxypropylmethylcellulose 1.5 % mass crosslinking catalyst – citric acid. For the analysis of rheological properties, hydroxypropylmethylcellulose solutions at different concentrations of humic substances (5, 10, 15 % by weight) were obtained.

The viscosity was determined according to ISO 2431³⁰. The method is based on determining the viscosity of a solution with free flow is taken

³⁰ ISO 2431 Paints and varnishes – Determination of flow time by use of flow cups. URL: <https://standards.globalspec.com/std/13356755/iso-2431>

as the time of continuous flow in seconds of a volume of 50 cm³ of the test material through a calibrated nozzle with 4 mm diameter of a Z-246 viscometer at a certain temperature.

Conductometric studies were carried out on a combined TDS-meter HM digital COM-100 (USA), scale range:

- Specific conductivity: from 0 to 9990 mks/cm;
- Temperatures: from 0 to 55 °C;
- Error: ± 2 %.

The melting point was determined according to GOST 25183.4-82³¹. The method is based on determining the temperature at which the gelatin jelly turns into a fluid state.

The destruction temperature was determined according to the method³². The destruction temperature is determined on a brass disc with a diameter of 50 mm and a thickness of 20 mm, equipped with a tin thermometer.

The determination of the gelation time took place in accordance with GOST 22181-91³³. The essence of the method is as follows. Prepare the resin mixture at 25 °C with the specified amount of the standard accelerator and initiator. The resulting mixture is placed in a test tube of established dimensions, which is immersed in a bath with a temperature of 25 °C.

Determination of water absorption of biofilm samples in cold water was performed according to ISO 62:2008³⁴. To determine the water absorption in cold water, samples of plastics in the form of disks or squares with a side of 50 mm are dried at 105 °C for one hour (if the polymer is resistant to 110 °C). After drying, the samples are cooled in a desiccator over calcium chloride and weighed. They are then placed in a vessel with distilled water so that the samples are completely covered with water and do not touch each other or the walls of the vessel. The samples are kept in water at a temperature of 22 °C for 24 hours, then removed from the water, wiped with filter paper and weighed.

Water absorption is calculated in mg/g the addition of sample X_1 by weight of the dried sample before immersion in water X_2 according to the formulas:

³¹ Photographic gelatin. Method for determining viscosity and viscosity drop, GOST 25183.4-82 (1982).

³² Podgornaya L. P. Theory and methods of research and testing of plastics, adhesives and sealants: textbook. way. / L. P. Podgornaya, G. M. Cherkashyna, V. V. Lebedev. Kharkiv : Textbook of NTU "KhPI", 2012. 268 p.

³³ Unsaturated polyester resins. Methods for determining the time of gelatinization, GOST 22181-91 (1991).

³⁴ ISO 62:2008. Plastics – Determination of water absorption

$$X_1 = \frac{m_1 - m}{m} \quad (1)$$

where m is the mass of the dried sample before immersion in water, g; m_1 – mass of the sample after being in water, g.

The tensile properties of biofilms were determined according to ISO 527-2:2012³⁵. The tests were performed on aursting machine IP 5040-5 in the mode of uniaxial stretching at a temperature of 22 °C. The test speed of the samples is 25 mm/min. Relative elongation at break (%) and Tensile strength (MPa) were determined.

Swelling of polymer hydrogels was performed in water solutions. The degree of swelling was calculated by the formula²⁸:

$$Q = 100 \left(\frac{m_1 - m}{m} \right). \quad (2)$$

where m_1 is the mass of the swollen sample, g; m is the mass of the sample before aging in water solution, g.

The adsorption activity of hydrogels A was defined as the ability to sorb Congo-red dye from water solution. To determine the adsorption activity used a solution of Congo-red concentration of 0.001 mol/l. A portion of the hydrogel m , g, was injected with a solution of Congo-red, taken in the amount of V , ml, and stirred for 2 hours.

Next, the solution was then centrifuged and spectrophotometrically determined ($\lambda = 498$ nm, SF-20 (LOMO)) Congo-red concentration in the supernatant. Calculation A was performed according to the following formula:

$$A = 100 \left(\frac{(C_0 - C_p) * v}{C_0 * m} \right) \quad (3)$$

where C_0 and C_p are initial and equilibrium Congo-red concentrations.

3. Results and discussion

Figures 2–4 show graphical dependences of the conditional viscosity of hydrogel solutions on the concentration of humic acid in them, obtained from various coal samples, and on the exposure time.

³⁵ ISO 527-2:2012. Plastics – Determination of tensile properties. Part 2: Test conditions for moulding and extrusion plastics.

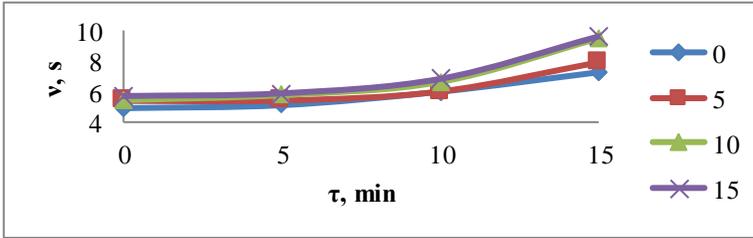


Fig. 2. Dependence of the conditional viscosity of the hydrogel on the content of humic acid obtained from sample No 1

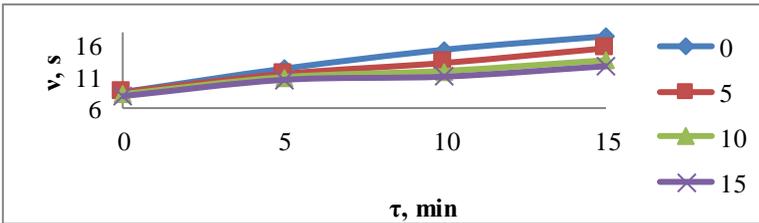


Fig. 3. Dependence of the conditional viscosity of the hydrogel on the content of humic acid obtained from sample No 2

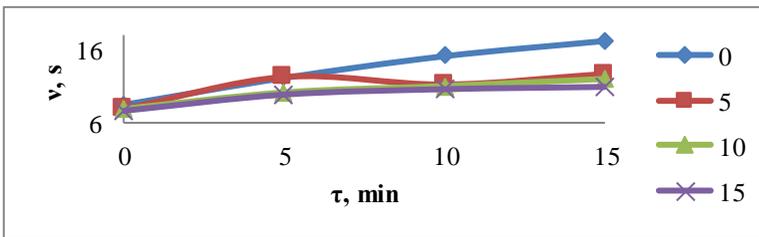


Fig. 4. Dependence of the conditional viscosity of the hydrogel on the content of humic acid obtained from sample No 3

Analyzing the graphical relationships, it can be concluded that an increase in the degree of metamorphism of the initial coals, expressed by an increase in the volatile matters and the oxygen content, leads to an increase in the dynamic viscosity of the hydrogel. It is of interest to determine, in addition to the factors describing the degree of coal metamorphism, the influence of the exposure time and the concentration of humic acids.

In fig. 5 shows a graphical dependence of the melting point of aydrogel with a concentration of humic acids from 0 to 15 %.

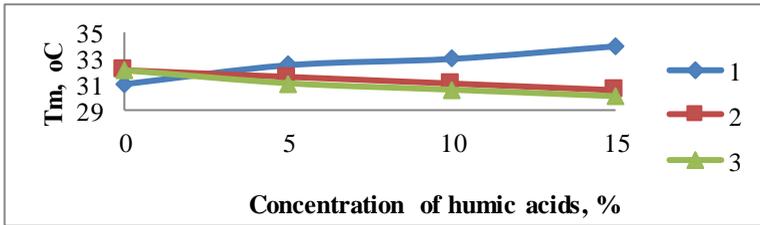


Fig. 5. Graphical dependence of the melting point of the hydrogel on the concentration of humic acids in it

Analyzing the above graphs, it can be concluded that an increase in the concentration of humic acids, depending on the properties of the original coals, leads to both an increase (sample 1) and a decrease (sample 2 and 3) of the hydrogel melting temperature.

In fig. 6 shows a graphical dependence of the degradation temperature of the hydrogel on the concentration of humic acids in it.

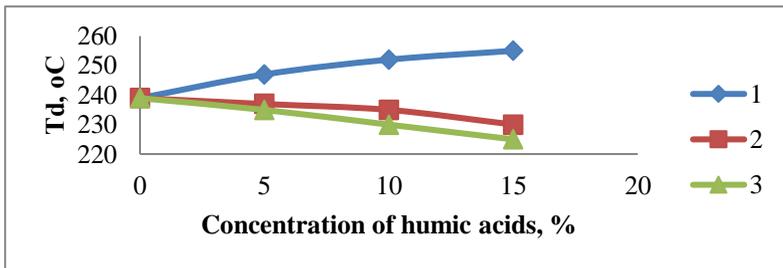


Fig. 6. Graphical dependence of the temperature of hydrogel destruction on the concentration of humic acids in it

Analyzing the graphs presented, it can be concluded that an increase in the concentration of humic acids, depending on the properties of the original coals, leads to both an increase (sample 1) and a decrease (samples 2 and 3) of the hydrogel destruction temperature.

In fig. 7 shows a graphical dependence of the gelatinization time of the hydrogel on the content of humic acids in it.

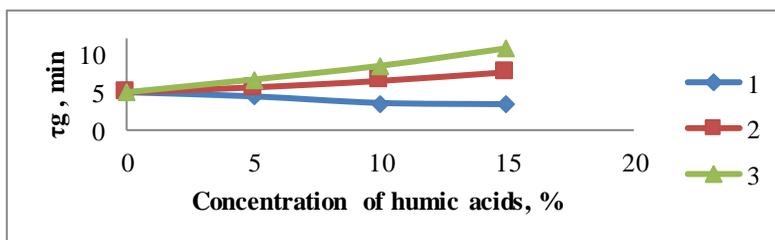


Fig. 7. Graphical dependence of the gelatinization time of the hydrogel on the concentration of humic acids in it

Analyzing the graphs presented, it can be concluded that an increase in the concentration of humic acids, depending on the properties of the initial coals, leads to both an increase (sample 2, 3) and a decrease (sample 1) of the gelatinization time of the hydrogel.

Summarizing the data on the effect of humic acids on the processes of structure formation in polymer hydrogels based on gelatin, it is important to emphasize its different nature for different hydrogels. So, for hydrogels with the addition of humic acids of sample 1, an intensifying structure-forming effect is clearly visible: the viscosity and the temperature of destruction increase with a decrease in the gelation time. At the same time, in hydrogels with the addition of humic acids in samples 2 and 3, an opposite pattern is observed, and they are inhibitors of the processes of structure formation in gelatin hydrogels.

To clarify the reasons for such a different nature of the effect of the studied humic acids, microscopic studies of the obtained hydrogels were carried out, the results of which are shown in Fig. 8. From the analysis of the obtained micrographs of the studied gelatin hydrogels with different contents of samples of humic acids, the different nature of the stay of humic acids in gelatin hydrogels was determined for three types of samples under study. Thus, sample 1 is characterized by the formation of a homogeneous transparent hydrogel, which, with an increase in the content of humic acids, only changes its color to a more yellow one. At the same time, for hydrogels obtained with the addition of samples of 2 and 3 humic acids, the presence of larger particles of coal (up to 1.0 mm) in the mass of samples is observed. In our opinion, it is the presence of larger coal particles in samples 2 and 3 that causes a decrease in the processes of structure formation in gelatin hydrogels by preventing the formation of a spatial network structure in them. On the contrary, the introduction of humic acids of sample 1 into the composition of gelatin hydrogels, for which the presence of particles of coal residues of various degrees of dispersion is not observed, causes an increase in the processes of structure formation.

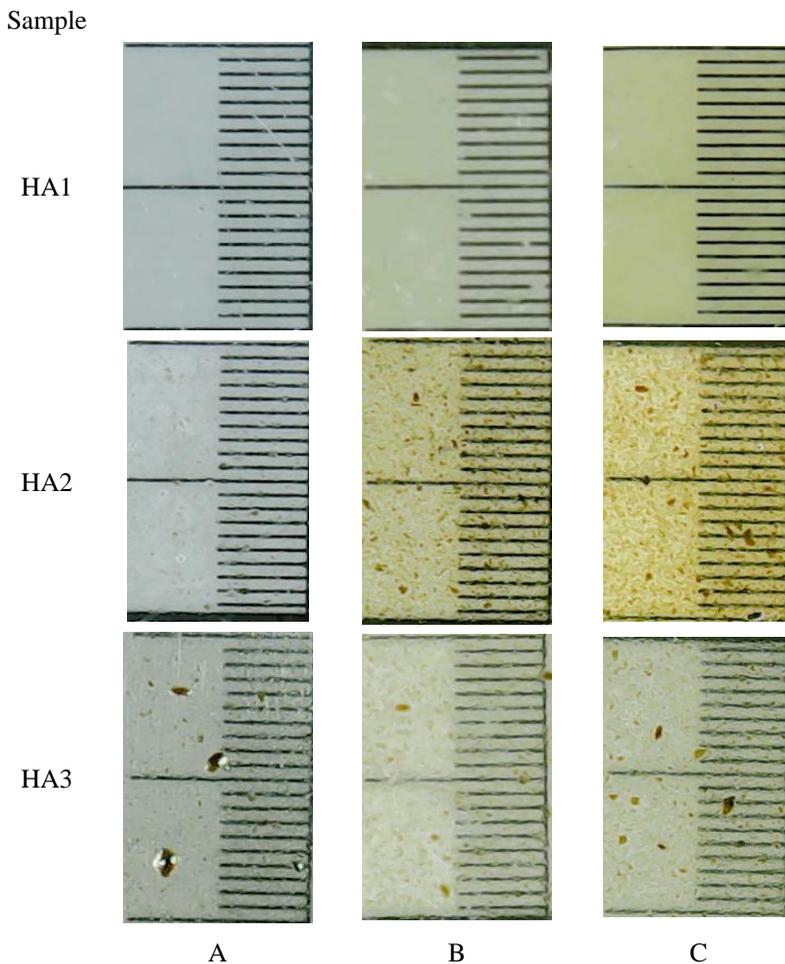


Fig. 8. Micrographs (DIV = 1 mm) of the investigated polymer hydrogels of gelatin with different content of humic acid:

A – polymer hydrogel of gelatin with 5 % humic acids;

B – polymer hydrogel of gelatin with 10 % humic acids;

C – polymer hydrogel of gelatin with 15 % humic acids

Table 7 shows the properties of polymer hydrogels based on gelatin, modified with humic acids.

Table 7 shows that the modification of polymer hydrogels based on gelatin with humic acids allows to obtain polymer hydrogels with high

swelling and adsorption activity and give them antibacterial properties, as evidenced by data on the time of appearance of mold in them.

Table 7

Properties of polymer hydrogels based on gelatin, modified with humic acids

Type and content of humic acids, % wt.	The degree of swelling, % wt.	Time of appearance of mold, hour	Adsorption activity A, mg/g
Composition without HA	26.5	24	1.7
HA1	5	80	3.1
	10	100	3.5
	15	120	3.7
HA2	5	100	4.1
	10	125	4.3
	15	150	4.6
HA3	5	Does not appear	4.8
	10	Does not appear	5.0
	15	Does not appear	5.1

In Fig. 9–11 show the dependences of the conditional viscosity of the mixtures on the duration and amount of HA or all three acids obtained from different coal samples.

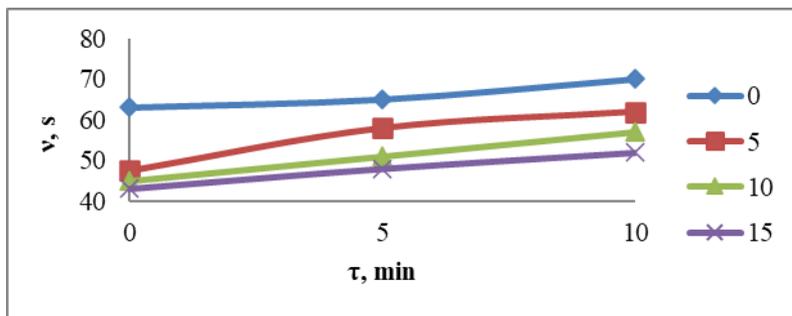


Fig. 9. Dependence of the conditional viscosity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No 1

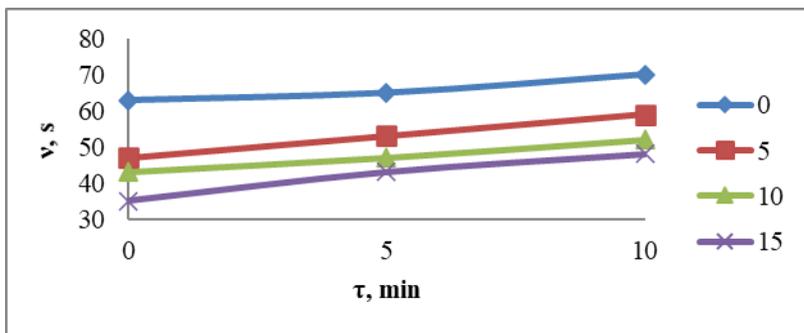


Fig. 10. Dependence of the conditional viscosity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No 2

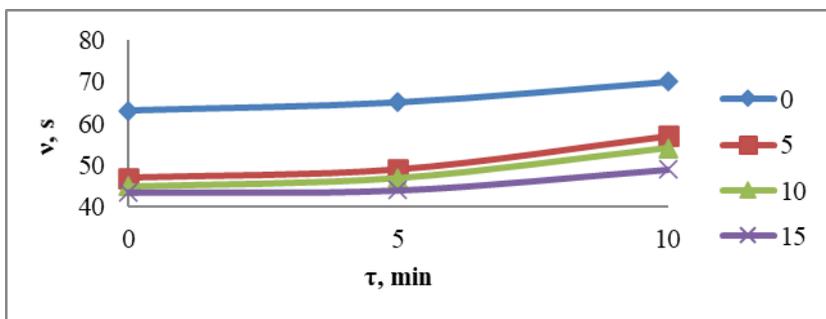


Fig. 11. Dependence of the conditional viscosity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No 3

From Fig. 9–11 it is seen that the introduction of all the studied types of humic acids in PVA solutions causes a decrease in their conditional viscosity due to the introduction of an additional amount of diluent, because humic acids are administered in the form of 8.5 % solutions in caustic soda. The diluting effect of humic acids increases in the series $HA1 < HA3 < HA2$.

In Fig. 12–14 are presented graphical dependences of the specific conductivity of polyvinyl alcohol solutions on the content of different types of humic acids.

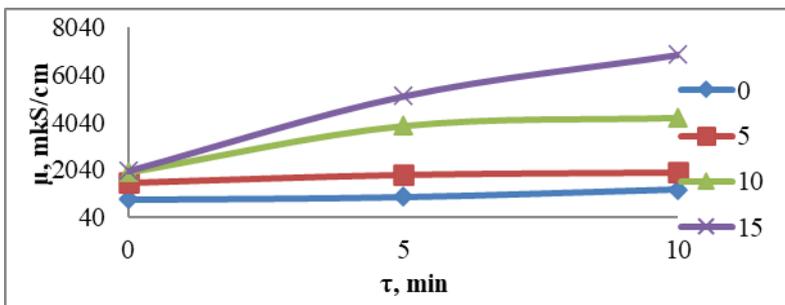


Fig. 12. Dependence of conductivity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No 1

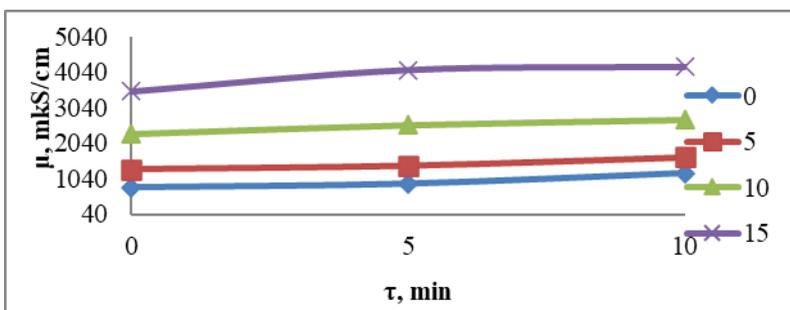


Fig. 13. Dependence of conductivity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No 2

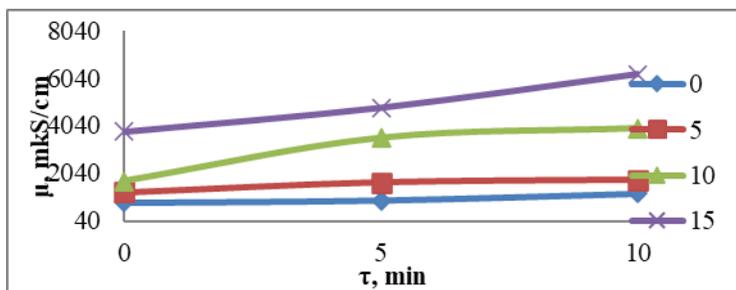


Fig. 14. Dependence of conductivity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No 3

Figs. 12–14 show that the introduction of humic acid solutions into PVA solutions enhances the processes of structure formation, which leads to an increase in the specific conductivity of polyvinyl alcohol solutions with

an increase in the content of different types of humic acids. The structure-forming effect of different types of humic acids decreases in number of HA1 > HA3 > HA2.

Studies have shown that humic acids have a specific effect on the processes of structure formation in PVA solutions, which is due to the different nature and characteristics of humic acids. Thus, for PVA solutions with the addition of humic acids, in which there are particles of coal residues of different degrees of dispersion or the combination of the acids themselves, clearly slows down the structuring effect. The formation of such particles is explained by the presence in samples HA2 and HA3 of a large number of oxygen-containing surfactants, which are able to form weak chemical and/or physical bonds with each other and with coal particles, which leads to relatively large aggregates. At the same time, in PVA solutions with the addition of humic acids with the absence of particles of coal residues of different degrees of dispersion, there is an increase in the processes of structure formation.

Table 8 shows the performance properties of biofilms based on polyvinyl alcohol modified with humic acids.

Table 8

**Performance properties of biofilms based
on polyvinyl alcohol modified with humic acids**

The content of humic acids, % wt.	Water absorption, % wt.	Tensile strength, MPa	Relative elongation at break, %	Time of appearance of mold, hour	
Composition without HA	220	20.0	18	24	
HA1	5	200	22.0	19	72
	10	190	23.0	20	84
	15	180	23.5	21	96
HA2	5	210	21.0	22	56
	10	200	21.5	23	68
	15	190	22.0	24	80
HA3	5	170	25.0	24	168
	10	160	27.0	25	Does not appear
	15	150	29.0	26	Does not appear

Table 8 shows that the modification of biofilms based on polyvinyl alcohol with humic acids permits to reduce their water absorption, increase the basic strength characteristics and give them antibacterial properties, as evidenced by data on the time of appearance of mold in the films. Thus, the modification of biofilms based on polyvinyl alcohol with humic acids allows obtaining strong waterproof films with antibacterial properties.

The graphical dependence of the conditional viscosity of hydroxypropylmethylcellulose solutions on the content of different types of humic substances is shown in Fig. 15.

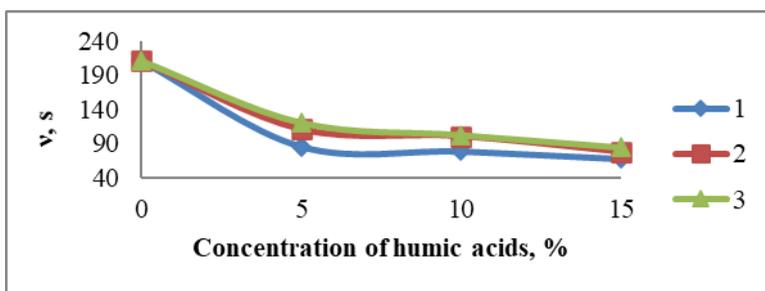


Fig. 15. The graphical dependence of the conditional viscosity of hydroxypropylmethylcellulose solutions on the content of different types of humic substances

Similar to the researches described above, the introduction of all investigated types of humic substances in hydroxypropylmethylcellulose solutions reduces its conditional viscosity due to the introduction of additional solvent, as humic substances are introduced in the form of 8.5 % by mass solutions. The action of the solvent of humic substances increases in number of HA1 > HA2 > HA3.

The processes of formation of structures by the method of conductometry were studied, the results of which are presented in Fig. 16–18 in the form of graphical dependences of specific electrical conductivity of hydroxypropylmethylcellulose solutions on the content of different types of humic substances.

The introduction of solutions of humic hydroxypropylmethylcellulose causes an increase in the intensity of structural processes, which leads to an increase in the specific conductivity of solutions of hydroxypropylmethylcellulose with increasing content of different types of humic substances. The effect of intensification of agglomeration processes in the studied samples of hydroxypropylmethylcellulose solutions is different

depending on the properties of humic substances and is similarly enhanced for the formation of number of HA3 > HA2 > HA1.

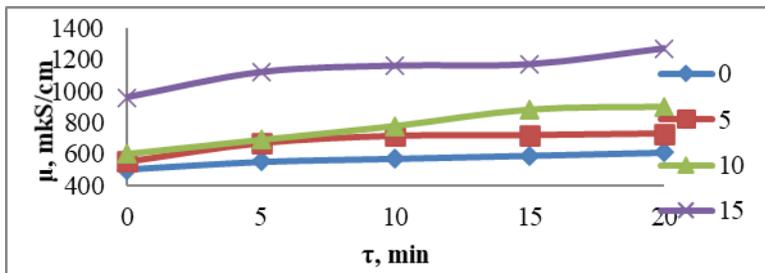


Fig. 16 Dependence of the specific conductivity of hydroxypropylmethylcellulose solutions on the content of humic acid from sample № 1

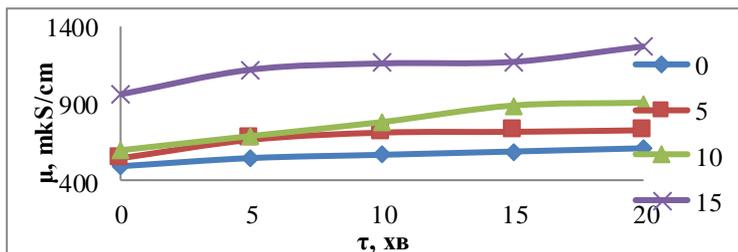


Fig. 17. Dependence of the specific conductivity of hydroxypropylmethylcellulose solutions on the content of humic acid from the sample № 2

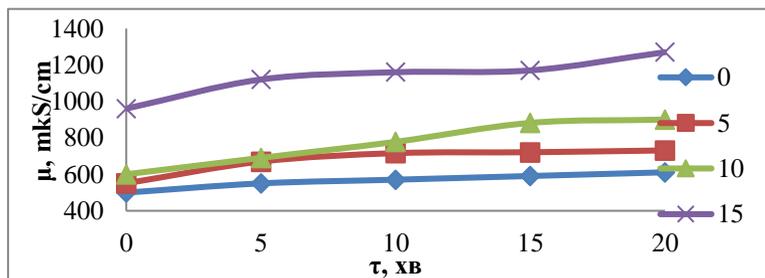


Fig. 18. Dependence of the specific substance of hydroxypropylmethylcellulose solutions on the content of humic acid from the sample No. 3

Table 9 shows the performance properties of biofilms based on hydroxypropylmethylcellulose modified with humic acids.

Table 9

**Performance properties of biofilms
based on hydroxypropylmethylcellulose modified with humic acids**

The content of humic acids, % wt.	Water absorption, % wt.	Tensile strength, MPa	Relative elongation at break, %	Time of appearance of mold, hours	
Composition without HA	430	10.0	12	48	
HA1	5	400	12.0	13	124
	10	390	13.0	14	148
	15	380	13.5	15	166
HA2	5	410	11.0	15	148
	10	400	11.5	17	166
	15	390	12.0	18	190
HA3	5	370	15.0	16	214
	10	360	17.0	19	Does not appear
	15	350	19.0	21	Does not appear

Table 9 shows that the modification of biofilms based on hydroxypropylmethylcellulose with humic acids permit to reduce their water absorption, increase the basic strength characteristics and give them antibacterial properties, as evidenced by data on the time of mold in the films. Thus, the modification of biofilms based on hydroxypropylmethylcellulose with humic acids allows obtaining strong water-soluble films with antibacterial properties for using as packaging for dry foods (bread, cereals, nuts, etc.) with extended shelf life.

CONCLUSIONS

This work proves the prospects and high efficiency of the use of humic substances in the processes of modification of polymers of different nature in order to obtain humic-polymeric materials.

It is noted that humic acids can have different effects on the processes of structure formation in polymers, due to the different nature and

characteristics of humic substances: the degree of metamorphism of the original coal, volatile matters and oxygen content.

It is desirable that humic acids do not contain a large amount of oxygen-containing surfactants that are able to form weak chemical and / or physical bonds with each other and with coal particles, which leads to relatively large aggregates in the structures of HA.

The presence of such aggregates can adversely affect the processes of polymer formation. At the same time in the solutions of polymers with the addition of humic acids in the absence of particles of carbon residues of varying degrees of dispersion, there is an increase in the processes of structure formation.

It is shown that the modification of polymer hydrogels based on gelatin with humic acids allows obtaining polymer hydrogels with a high degree of edema and giving them antibacterial properties, which is confirmed by the data on the time of appearance of mold in them.

It was found that the modification of biofilms based on polyvinyl alcohol and hydroxypropylmethylcellulose permits to reduce their water absorption, increase the basic strength characteristics and give them antibacterial properties, which is confirmed by data on the time of appearance of mold in films. In general, the modification of biofilms with humic acids allows obtaining strong water-resistant films with antibacterial properties, which can be used, including for packaging dry food products (bread, cereals, nuts, etc.) with extended shelf life.

SUMMARY

Effective ways of using low-grade coal with a low degree of metamorphism in order to obtain humic acids, which will be used for the modification of bioplastics and polymer hydrogels, were considered. Humic acids have a specific effect on the processes of structure formation in polymers, due to the different nature and characteristics of humic substances: the degree of metamorphism of the original coal, the volatile matters and oxygen content. It is established that the modification of polymer hydrogels based on gelatin with humic acids allows to obtain polymer hydrogels with a high degree of edema and give them antibacterial properties, which is confirmed by data on the time of appearance of mold in them. As a result of research on the modification of humic substances, packaging biodegradable films based on polyvinyl alcohol and hydroxypropylmethylcellulose with antibacterial properties were obtained. These films are suitable for packaging dry food products (bread, cereals, nuts, etc.) with a long shelf life.

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SYMBOLS

W^a – moisture contents, %;
 A^d – ash content, %;
 S_t^d – content of sulfur, %;
 V^d – volatile matter, %;
 C^d – content of carbon, %;
 H^d – content of hydrogen, %;
 O^d – content of oxygen, %;
 $(HA)^{daf}_t$ – total mass fraction of humic acids, %;
 $(HA)^{daf}_f$ – yield of free humic acids, %;
 SiO_2 – content of silicon oxide, %;
 Al_2O_3 – content of aluminium oxide, %;
 Fe_2O_3 – content of iron oxide, %;
 MgO – content of magnesium oxide, %;
 CaO – content of calcium oxide, %;
 Na_2O – content of sodium oxide, %;
 K_2O – content of potassium oxide, %;
 SO_3 – content of sulfur oxide, %;
 v – conditional viscosity, s;
 T_m – melting temperature, °C;
 T_d – decomposition temperature, °C;
 τ_g – gelation time, min.

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