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Use of Humic Acids from Low-Grade Metamorphism Coal for the Modification of Biofilms Based on Polyvinyl Alcohol

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Abstract

Humic acids (HA) were extracted from three different samples of low-grade Ukrainian coal. Polyvinyl alcohol (PVA) solutions modified with HA of different origin were obtained, which are planned to be used to obtain biodegradable bactericidal resistant films. Studies of the influence of humic acids on the processes of structure formation in PVA solutions have been carried out, on the basis of which it has been shown that they are due to different nature and characteristics of humic acids: presence or absence of coal residue particles.

***Keywords**: Coal, Lignite; Humic acids; Biodegradable bactericidal resistant films; Polyvinyl alcohol.*

1. Introduction

Currently, one of the most relevant areas of the latest developments in the packaging industry is to obtain materials that would combine a high level of basic performance (strength, gas and/or moisture resistance) with the ability of packaging waste to biodegrade [1]. Modern research in the field of biodegradable materials, including packaging, is conducted in two main areas:

- Development of compositions of polymeric materials with addition of auxiliary substances which under the influence of microorganisms would quickly decompose and completely mineralize (thus polymers can be made both from petrochemical, and from renewable raw materials of a vegetable or animal origin);
- Synthesis of polymeric materials with properties for rapid decomposition [2].

Based on the method of production, currently used biodegradable packaging materials are divided into:

- Materials obtained by synthetic means;
- Materials based on natural polymers obtained by biological modification of the latter;
- The use of additives that give synthetic polymers the ability to decompose into safe components during disposal.

On the other hand, humanity has recently been in a period of global pandemic caused by the coronavirus COVID-19, so almost every inhabitant of the planet is faced with the need to use antibacterial masks and hygiene products. This problem is no less relevant in terms of the use of various packaging and packaging materials. In recent years, there has been a significant increase in the use of various bactericidal and fungicidal additives in polymers in Western Europe and the Americas, especially in the medical sector, the production of food-contact packaging. That is why the current state of the food industry and the direction of development of food technologies are aimed at improving the quality of food and harmonizing measures for food storage, taking into account food safety indicators. Domestic and foreign researchers are working fruitfully to develop modern technologies for antibacterial packaging. General directions of research can be classified as follows:

- Inclusion of antimicrobial substances in the package from which volatile biologically active substances are released during storage;
- Direct inclusion of antimicrobial agents in the packaging film;
- Coating the package with a matrix that behaves as a carrier for the antimicrobial agent and can release antimicrobial agents on the surface of the product.

That is why solving the problems of microbiological contamination of packaging from biodegradable polymeric materials in the food industry by expanding the range of packaging biofilms with bactericidal properties is very important.

Biodegradable films with antibacterial effect today have a limited distribution, but in the scientific literature there is data on their production. Films based on starch or polylactic acid, which increase the preservation of green pepper and minimally processed lettuce, are described in [3-4]. It is indicated that the addition of essential oil as an antimicrobial agent can help improve the performance of biodegradable films in food preservation. Studies [4-5] have confirmed that the addition of antimicrobials, such as clove essential oil or oregano, has reduced the amount of yeast, mold and bacteria in starch films. It has also been found [6] that mixing starch with polyvinyl alcohol (PVA) and alginate (triple mixture of polymers) allows to obtain films that were more resistant to stretching, less permeable to water vapor and less hydrophilic than films containing only starch. A very promising synthetic material for the production of packaging biofilms with bactericidal properties is PVA - a universal polymer with a large industrial application, which is obtained only by synthesis; the main chain of PVA contains CC bonds that promote rapid biodegradation [7-9].

Thus, combining two actually opposite characteristics in a packaging polymeric material - bioresistance to microorganisms and biodegradability - is a very difficult task. In fact, it is necessary to obtain a packaging material that, during the period of use, will be resistant to the action of various bacteria and even prevent their occurrence, and in the future this same material should already have the ability to biodegradation.

Seemingly, humic acids, like, for a call, get rid of the low levels of metamorphism (which is more important, the storm of the metamorphism, according to the one, - lignite), have a number of antibacterial powers. In the world (including Ukraine) there are significant deposits of lignite (brown coal) and hard coal of low metamorphism degree. Currently, lignite has a very limited use due to poor technological characteristics (high ash, water and sulfur contents). Lignite is proposed to be used in the oxidative desulfurization process [10-13], to obtain components of boiler fuels or bitumen [14], in gasification processes [15]. However, the direction of application of brown coal seems to be the most promising for the extraction of humic acids and subsequent production of polymer materials.

Therefore, it is promising to obtain packaging biofilms with bactericidal properties based on PVA using an antibacterial additive of humic acids. On the other hand, in the scientific and patent literature there are many different types of possibilities for the approval of spills on the basis of PVA, at the warehouse of which biologically active substances were included. From the same point, the purpose of this article is to study the features of the influence of humic acids on the processes of structure formation of solutions of polyvinyl alcohol for the production of biofilms.

2. Experimental part

2.1. Raw materials

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. For the acquisition of humic acids, they were taken to a low level of metamorphism, the characteristics of which are given in Tables 1-3.

As can be seen from the obtained characteristics, primarily according to V^{daf}, coal № 1-3 according to the accepted classification [16] belongs to lignite. Sample № 1 is characterized by abnormally low humidity, which is explained by the relatively low oxygen content (per organic part).

Table 1. Proximate analysis of 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)

Table 2. Ultimate analysis of organic mass of coal

Sample	Ultimate analysis, % mas				
	C^{daf}	H^{daf}	N^{daf}	S^{daf}_t	O^{daf}_d
1	80.83	4.48	1.29	2.50	10.90
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 $(HA)^{daf}_t$ and yield of free humic acids $(HA)^{daf}_f$

Sample	$(HA)^{daf}_t$, %	$(HA)^{daf}_f$, %
1	87.60	79.44
2	49.66	44.27
3	82.94	75.30

2.2. Experimental techniques

Humic acid was obtained according to [17]. 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.

Solutions of polyvinyl alcohol with a concentration of 10% obtained by dissolving the polymer in a mass 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. Then, samples of 50 cm^3 were taken from the solutions.

Conductometric studies of polyvinyl alcohol solutions were carried out on a combined TDS-meter HM digital COM-100 (USA), scale range: specific conductivity: from 0 to 9990 µS/cm; temperatures: from 0 to 55°C; error: ± 2%.

Microscopic studies were carried out using the electron microscope Digital Microscope HDcolor CMOS Sensor (China).

The viscosity was determined according to ISO 2431 [18]. The method is based on determining the viscosity of a solution with free flow is taken as the time of continuous flow in seconds of a volume of 50 cm^3 of the test material through a calibrated nozzle with 4 mm diameter of a VZ-246 viscometer at a certain temperature.

2.3. Mathematical processing of results

On the basis of these experimental results, experimental-statistical mathematical models (an equal regression) were developed. For the knowledge of the performance of many regressions, such as describing the deposits and functions in response to the process by officials, the STATISTICA application package is chosen. Evaluation of the adequacy of the statistical significance of the regressions was successful [19-21].

The estimation of model adequacy is conducted using the following parameters: the mean relative error of approximation (ε_i); the coefficient of determination (R_i^2); Fisher criterion (F_i), and criterion of statistics (F_{r_i}). To estimate the adequacy of the obtained regression equations, we substituted the given experimental parameters (X_{ij}) and found the expected (regressive) values of response functions (Y_{ij}^{reg}).

The coefficient of determination (R^2), which characterizes the significance of the accumulation of functions in the response (Y) in the process (X) and in the swelling value from

0 to 1, was based on the standard methods [20]. The value of mean relative error of approximation was calculated by the formula (1):

$$\varepsilon_i = \frac{1}{n}\sum_{j=1}^{n}\left|\frac{Y_{ij} - Y_{ij}^{reg}}{Y_{ij}}\right| \qquad (1)$$

where n is the amount of sampling (number of experiments), Y_{ij} – values observed during the experiments, Y_{ij}^{reg} – values of response functions calculated using the regression equations, i is response function number, and j is experiment number.

To check the adequacy of multiple-factor regressive model we used Fisher criterion. It was calculated by the formula:

$$F = \frac{S_{reg_i}^2}{S_{res_i}^2}, \qquad (2)$$

where $S_{reg_i}^2$ is dispersion of experimental response functions relative to their mean values and $S_{res_i}^2$ is residual dispersion of response functions.

$$S_{res_i}^2 = \frac{1}{n-1}\sum_{j=1}^{n}(Y_{ij} - \overline{Y}_i)^2 \qquad (3)$$

where $\overline{Y}_i$ is average experimental value of response function.

$$S_{res_i}^2 = \frac{1}{n-m_i}\sum_{j=1}^{n}(Y_{ij}^{reg} - Y_{ij})^2 \qquad (4)$$

where m_i is number of coefficients in the regression equation.

In accordance with the mentioned calculations Fisher criterion should be greater than the table value at the significance level α and numbers of freeness (n-1) and (n – m_i). In such a case it means the quantitative change of results scattering relative to the line of obtained regression equation compared with scattering relative to the mean value [19].

3. Results and discussion

For the purpose of modifying polymeric compositions based on PVA with humic acids, it is planned to develop until ready biodegradable pills for the manifestation of hybrids - health until antibacterial during the period. At the same time, it is very important to think that the modification of polyvinyl alcohol with humic acids is injected into the food for the possibility of a positive approval by the amount of PVA and HA biofuel (injecting the amount of HA into the process). Fig. 1 shows micrographs of humic acid solutions.

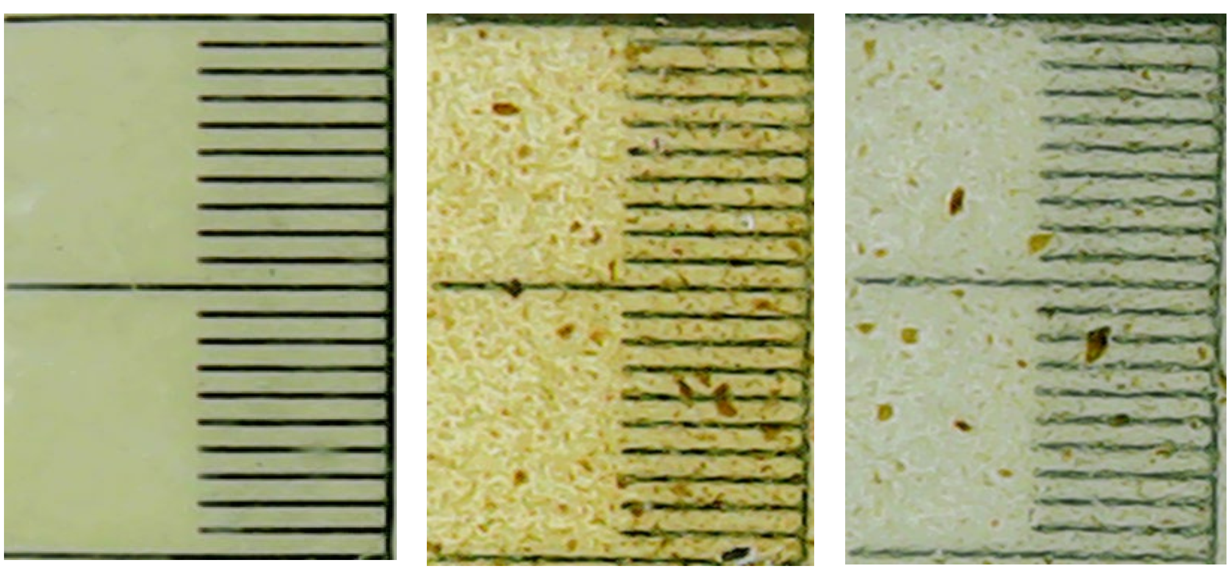

Fig. 1. Micrographs (one division of the graduated scale is 1 mm) of humic acids

From the analysis of the obtained micrographs of the studied humic acids, the presence of conglomerates of different degrees of dispersion in the HA2 and HA3 samples was determined, which is largely due to the difference in the stages of isolation of the studied humic acids: pure whole solution was used for HA1. The presence of conglomerates, in our opinion, is also due to the fact that humic acids in samples HA2 and HA3 are presented in the form of polydisperse heteropolymers with a higher molecular weight [22] than in the sample HA1, which contributes to the formation of the above conglomerates. On the contrary, in HA1, which was characterized by a relatively low content of oxygen compounds, microphotographs show no noticeable accumulations of conglomerates. Also, this difference 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, which leads to the appearance of relatively large aggregates.

In the Table 4 presents the results of studying the effect of the amount of HA and the duration of preparation of modified PVA solutions on the viscosity of the obtained products. In the same place (Table 4) process factors (HA content in a mix, duration, quality of initial coal) are resulted. Also in Figs. 2-4 show the dependences of the conditional viscosity of the mixtures on the duration and amount of HA for all three acids obtained from different coal samples.

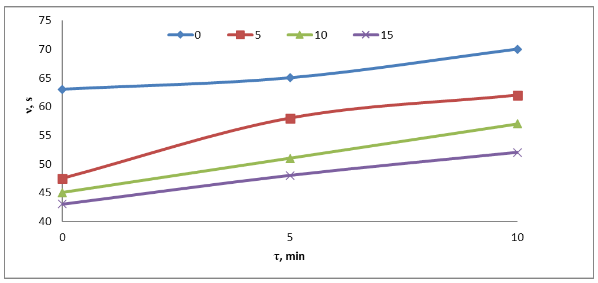

Fig. 2 Dependence of the conditional viscosity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No. 1

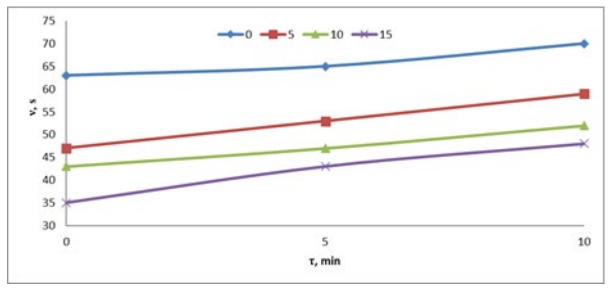

Fig. 3 Dependence of the conditional viscosity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No. 2

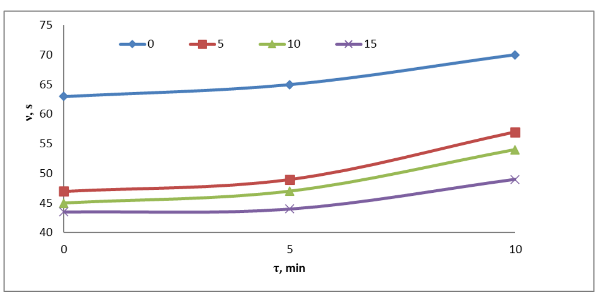

Fig. 4 Dependence of the conditional viscosity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No. 3

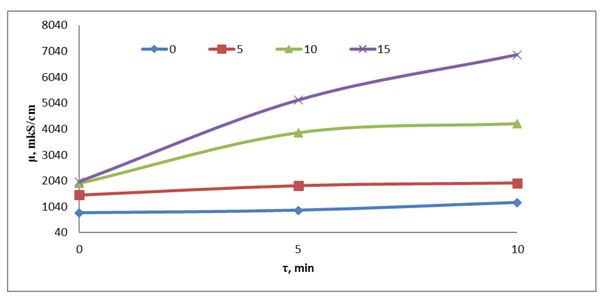

Fig. 5. Dependence of conductivity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No. 1

From Table 4 and Figs. 2-4 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. Summarizing the main aspects of the effect of humic acids on the viscosity characteristics of the studied solutions of polyvinyl alcohol, it can be noted that their diluting effect can potentially facilitate further processes of obtaining thin and strong biodegradable films with antibacterial properties.

Table 4. Experimental and calculated (regression) values of the conditional viscosity (CV) of PVA before and after their modification HA

№	CV, v, s (experimental values, Yij)	Factors (X_{ij})					v^{reg}, s (calculated values, Y^{reg}_{ij})		
		HA, %	τ, min	V^d, %	C^{daf}, %	O^{daf}_d, %	v^{reg}_{1j} = f (HA, τ, V^d)	v^{reg}_{2j} = f (HA, τ, C^{daf})	v^{reg}_{3j} = f (HA, τ, O^{daf}_d)
1.	63.0	0	0	29.1	80.83	10.90	60.4	60.0	60.2
2.	47.5	5	0	29.1	80.83	10.90	53.7	53.3	53.5
3.	45.0	10	0	29.1	80.83	10.90	47.0	46.6	46.7
4.	43.0	15	0	29.1	80.83	10.90	40.3	39.9	40.0
5.	65.0	0	5	29.1	80.83	10.90	65.2	64.8	65.0
6.	58.0	5	5	29.1	80.83	10.90	58.5	58.1	58.2
7.	51.0	10	5	29.1	80.83	10.90	51.8	51.4	51.5
8.	48.0	15	5	29.1	80.83	10.90	45.1	44.7	44.8
9.	70.0	0	10	29.1	80.83	10.90	70.0	69.6	69.8
10.	62.0	5	10	29.1	80.83	10.90	63.3	62.9	63.0
11.	57.0	10	10	29.1	80.83	10.90	56.6	56.2	56.3
12.	52.0	15	10	29.1	80.83	10.90	49.8	49.5	49.6
13.	63.0	0	0	43.7	68.10	24.11	57.7	58.4	58.2
14.	47.0	5	0	43.7	68.10	24.11	51.0	51.7	51.5
15.	43.0	10	0	43.7	68.10	24.11	44.3	45.0	44.8
16.	35.0	15	0	43.7	68.10	24.11	37.6	38.2	38.1
17.	65.0	0	5	43.7	68.10	24.11	62.5	63.2	63.0
18.	53.0	5	5	43.7	68.10	24.11	55.8	56.5	56.3
19.	47.0	10	5	43.7	68.10	24.11	49.1	49.7	49.6
20.	43.0	15	5	43.7	68.10	24.11	42.4	43.0	42.9
21.	70.0	0	10	43.7	68.10	24.11	67.3	68.0	67.8
22.	59.0	5	10	43.7	68.10	24.11	60.6	61.2	61.1
23.	52.0	10	10	43.7	68.10	24.11	53.9	54.5	54.4
24.	48.0	15	10	43.7	68.10	24.11	47.2	47.8	47.7
25.	63.0	0	0	43.7	60.71	29.12	57.7	57.4	57.5
26.	47.0	5	0	43.7	60.71	29.12	51.0	50.7	50.7
27.	45.0	10	0	43.7	60.71	29.12	44.3	44.0	44.0
28.	43.5	15	0	43.7	60.71	29.12	37.6	37.3	37.3
29.	65.0	0	5	43.7	60.71	29.12	62.5	62.2	62.2
30.	49.0	5	5	43.7	60.71	29.12	55.8	55.5	55.5
31.	47.0	10	5	43.7	60.71	29.12	49.1	48.8	48.8
32.	44.0	15	5	43.7	60.71	29.12	42.4	42.1	42.1
33.	70.0	0	10	43.7	60.71	29.12	67.3	67.0	67.0
34.	57.0	5	10	43.7	60.71	29.12	60.6	60.3	60.3
35.	54.0	10	10	43.7	60.71	29.12	53.9	53.6	53.6
36.	49.0	15	10	43.7	60.71	29.12	47.2	46.9	46.9
Average value	$\overline{v}(\overline{Y}_i)$=53.3	–	–	–	–	–	–	–	–

Table 5. Experimental and calculated (regression) values of conductivity of PVA before and after their modification HA

№	Conductivity, μ, mkS/cm (experimental values, Y_{ij})	Factors (X_{ij})					Conductivity, μ^{reg}, mkS/cm (calculated values, Y^{reg}_{ij})		
		HA, %	τ, min	V^d, %	C^{daf}, %	O^{daf}_d, %	μ^{reg}_{1j}= = f (HA, τ, V^d)	μ^{reg}_{2j} = = f (HA, τ, C^{daf})	μ^{reg}_{3j} = = f (HA, τ, O^{daf}_d)
1.	1500	5	0	29.1	80.83	10.90	1172	1059	1092
2.	1940	10	0	29.1	80.83	10.90	2490	2377	2410
3.	2000	15	0	29.1	80.83	10.90	3808	3695	3728
4.	900	0	5	29.1	80.83	10.90	639	526	559
5.	1850	5	5	29.1	80.83	10.90	1957	1844	1877
6.	3900	10	5	29.1	80.83	10.90	3275	3162	3195
7.	5150	15	5	29.1	80.83	10.90	4593	4480	4513
8.	1200	0	10	29.1	80.83	10.90	1424	1311	1344
9.	1950	5	10	29.1	80.83	10.90	2742	2629	2662
10.	4250	10	10	29.1	80.83	10.90	4060	3947	3980
11.	6900	15	10	29.1	80.83	10.90	5378	5265	5298
12.	1300	5	0	43.7	68.10	24.11	871	957	940
13.	2300	10	0	43.7	68.10	24.11	2189	2275	2258
14.	3500	15	0	43.7	68.10	24.11	3507	3593	3576
15.	900	0	5	43.7	68.10	24.11	338	424	407
16.	1400	5	5	43.7	68.10	24.11	1656	1742	1725
17.	2550	10	5	43.7	68.10	24.11	2974	3060	3043
18.	4100	15	5	43.7	68.10	24.11	4292	4378	4361
19.	1200	0	10	43.7	68.10	24.11	1123	1209	1192
20.	1640	5	10	43.7	68.10	24.11	2441	2527	2510
21.	2700	10	10	43.7	68.10	24.11	3759	3845	3828
22.	4190	15	10	43.7	68.10	24.11	5077	5163	5146
23.	1250	5	0	43.7	60.71	29.12	871	898	882
24.	1700	10	0	43.7	60.71	29.12	2189	2216	2200
25.	3800	15	0	43.7	60.71	29.12	3507	3534	3518
26.	900	0	5	43.7	60.71	29.12	338	365	349
27.	1650	5	5	43.7	60.71	29.12	1656	1683	1667
28.	3510	10	5	43.7	60.71	29.12	2974	3001	2985
29.	4800	15	5	43.7	60.71	29.12	4292	4319	4303
30.	1200	0	10	43.7	60.71	29.12	1123	1150	1134
31.	1750	5	10	43.7	60.71	29.12	2441	2468	2452
32.	3910	10	10	43.7	60.71	29.12	3759	3786	3770
33.	6200	15	10	43.7	60.71	29.12	5077	5104	5088
Average value	$\overline{\mu}(\overline{Y}_i)$=53.3	–	–	–	–	–	–	–	–

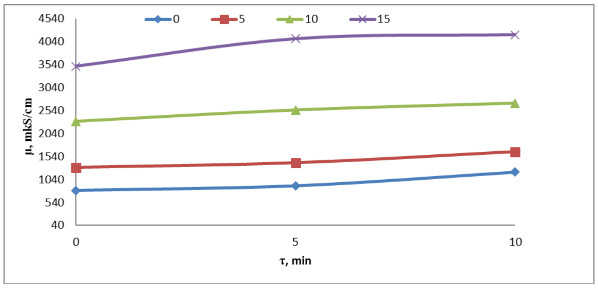

Fig. 6. Dependence of conductivity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No. 2

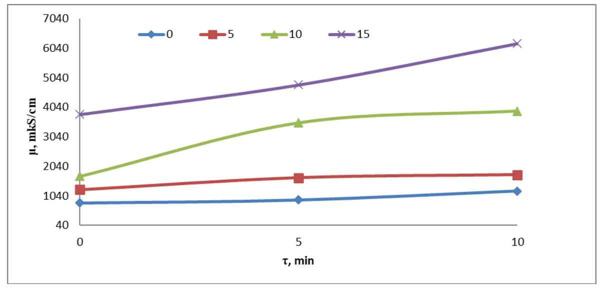

Fig. 7. Dependence of conductivity of the solutions of polyvinyl alcohol on the content of humic acid obtained from sample No. 3

Next, the processes of structure formation by the method of conductometry were studied, the results of which are presented in Table 5 and in the form of graphical dependences of the specific conductivity of polyvinyl alcohol solutions on the content of different types of humic acids (Figs. 5-7).

Figs. 5-7 and Table 5 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 a number of HA1>HA3>HA2.

First of all, the reason for such a slightly different influence on the structure of HA formation may be the presence of relatively large conglomerates in HA3 and, especially, HA2 (see Fig. 1). The presence of coal particles and/or aggregates of HA of different degrees of dispersion cause a decrease in the processes of structure formation in PVA solutions by preventing the formation of a spatial mesh structure. On the contrary, the introduction into the composition of PVA solutions of humic acids of the HA1 sample, for which the presence of particles of different sizes is not observed, causes the strengthening of the processes of structure formation.

Based on the obtained experimental data (see Tables 4, and 5), experimental-statistical mathematical models (ESMM) were created, which described the dependence of the conditional viscosity and conductivity of PVA on the HA content, cooking time and one of the characteristics of the raw material used to obtain humic acids. These equations are given in Tables 6, and 7. On the basis of the obtained equations, substituting the values of the factors in them, for each experiment we found the expected values of the response functions (Y_{ij}^{reg}) and the relative errors of the ESMM (ε). Their values are given in tables 4, 5 and 6, 7, respectively. Based on the regression values of the response functions, the adequacy of the models was checked by calculating the Fisher criterion, the values of which are also given in Tables 6, and 7.

Table 6. ESMM dependence of conditional viscosity of PVA solutions on process factors and characteristics of coal

No.	Equation type	Assessment of statistical significance and adequacy			
		R^2	R	ε, %	F
5	$\nu_1 = 65.7566 - 1.3422 \cdot HA + 0.9583 \cdot \tau - 0.1841 \cdot V^d$	0.892	0.944	4,70	8,45
6	$\nu_2 = 49.5644 - 1.3422 \cdot HA + 0.9583 \cdot \tau + 0.1294 \cdot C^{daf}$	0.886	0.941	4,89	8,04
7	$\nu_3 = 61.7911 - 1.3422 \cdot HA + 0.9583 \cdot \tau - 0.1489 \cdot O_d^{daf}$	0.888	0.942	4,74	8,17

Table 7. ESMM dependence of conductivity of PVA solutions on process factors and characteristics of source coal

No.	Equation type	Assessment of statistical significance and adequacy			
		R^2	R	ε, %	F
8	$\mu_1 = 799.1079 + 240.6444 \cdot HA + 128.3333 \cdot \tau - 18.9212 \cdot V^d$	0.821	0.906	28,03	5,37
9	$\mu_2 = -448.1379 + 240.6444 \cdot HA + 128.3333 \cdot \tau + 7.3336 \cdot C^{daf}$	0.816	0.903	26,43	5,18
10	$\mu_3 = 2.14487 - 0.11185 \cdot HA + 0.31978 \cdot \tau + 0.28304 \cdot O_d^{daf}$	0.817	0.904	26,80	5,22

The average relative errors ε indicate that the compliance of the constructed models for viscosity with experimental data can be considered high (when ε=0-10% - the accuracy of the prediction is high), for conductivity - satisfactory (ε=20-50%) [23].

Tabular critical values of Fisher's criterion at the level of significance α=0.05: for conditional viscosity F_{1cr}=1.60; for conductivity F_{2cr}=1.64 and are less than the calculated values given in Tables 7, and 8. Therefore, the obtained data indicate the adequacy of the developed linear ESMM.

The obtained regression equations allow us to state that any of the proposed main characteristics of low-grade metamorphism coal can be used to predict the quality of PVA solutions. Also on the basis of these equations it can be concluded that the increase in the degree of metamorphism of the source coal (increase in C^{daf}) causes, in the final case, the conditional viscosity and specific conductivity of PVA. The oxygen content of these indicators follows differently.

4. Conclusions

The conducted researches allowed receiving and investigating the PVA solutions modified with humic acids of various natures. 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. Adequate ESMMs have also been developed to predict viscosity and conductivity of PVA production factors and source coal characteristics.

The prospect of further research is to study biofilms obtained on the basis of PVA solutions modified with humic acids of various natures, for the most important performance characteristics.

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Symbols

W^a	*moisture contents, %;*	$(HA)^{daf}{}_t$	*total mass fraction of humic acids, %;*
A^d	*ash content, %;*	$(HA)^{daf}{}_f$	*yield of free humic acids, %;*
V^d	*volatile matter, %;*	v	*conditional viscosity, s;*
C^d	*content of carbon, %;*	μ	*conductivity, mkS/cm;*
H^d	*content of hydrogen, %;*	R^2	*the coefficient of determination, %;*
N^d	*content of nitrogen, %;*	R	*the coefficient of regression;*
$S^d{}_t$	*content of sulfur, %;*	ε	*the mean relative error of approximation, %;*
O^d	*content of oxygen, %;*	F	*Fisher criterion.*

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