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Hybrid Modification of Eco-Friendly Biodegradable Polymeric Films by Humic Substances from Low-Grade Metamorphism Coal

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Abstract

The peculiarities of the influence of humic substances on the processes of structure formation of hydroxypropyl methylcellulose solutions for obtaining hybrid ecologically pure biodegradable polymer films were investigated in the article. The modifying effect of humic substances, which were obtained from three different samples of low-grade Ukrainian coal, was studied. Hydroxypropyl methylcellulose solutions modified with humic substances of various origins were used to obtain ecologically pure biodegradable polymer films on their basis. A study of the influence of humic substances on the processes of structure formation in solutions of hydroxyethyl cellulose, on the basis of which it was shown that they are due to the different nature and characteristics of humic substances.

***Keywords**: Coal; Lignite; Humic substances; Biodegradable bactericidal resistant films; Hydroxypropyl methylcellulose.*

1. Introduction

Currently, the global trend is the production and use of environmentally friendly biodegradable polymeric materials, which implement the principle of "zero waste" throughout the life cycle - "production-use-disposal", so this class of polymers is widely used in the market today [1]. According to the method of production of environmentally friendly biodegradable polymeric materials, can be polymers that are directly derived from biomass of plant or animal origin (polysaccharides, proteins, lipids, etc.), as well as polymers obtained by classical chemical synthesis from renewable monomers on a biological basis, such as polylactic acid (PLA), or polymers obtained by natural or genetically modified microorganisms, such as polyhydroxyalkanoates (PHAs), polyhydroxybutyrates (PHBs), bacterial cellulose, xanthan, gelan, pullulan and others. The use of such a large range of environmentally friendly biodegradable polymer matrices allows obtaining materials with sufficient gas insulation characteristics, heat resistance, which can be processed into different products and parts for different industries [2].

Today, films, trays, coatings and other materials based on environmentally friendly biodegradable polymer matrices make it possible to use them as materials for packaging and other applications [3-5]. At the same time, the level of such characteristics as impact strength, heat resistance, gas permeability and antisepticity of environmentally friendly biodegradable polymeric materials often do not meet the requirements of the application conditions [2]. That is why it is promising to keep hybrid environmentally friendly biodegradable polymeric materials modified with reagents of inorganic and organic nature. Today, hybrid polymer-inorganic nanocomposites are used to obtain materials with semiconductor and superconducting properties, and hybrid modification of polymers allows obtaining composites of high fire resistance [6]. Most often, as hybrid modifiers of polymers, layered silicates of natural or synthetic origin montmorillonite, gallosite, silica, laponite, etc. are used hydrotalcite. In addition, as shown in publications [7-8], the inclusion of silicates in film biopolymers 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 modification of polymers with silicate substances, there are some problematic aspects related to the potential toxicity of modifications that should be considered when migrating from environmentally friendly biodegradable 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 others [9]. In general, carbon and carbon materials are now known as immobilized or included in the polymer matrix hybrid modifiers, which allow to obtain effective sorbents, ion exchange and antimicrobial materials for various industries: electronics, medicine, instrumentation and others. That is why it is promising to obtain hybrid environmentally friendly biodegradable polymeric materials modified with humic substances with two virtually opposite characteristics - bio resistance to microorganisms and the ability to biodegrade.

Lignite (brown coal) was used quite effectively in the oxidative desulfurization process [10-15] or in gasification processes [16-17]. However, the direction of application of brown coal seems to be the most promising for the extraction of humic acids and subsequent production of fertilizers or polymeric materials. Therefore, in our previous work [18], polymeric hydrogens modified with humic substances were obtained. It is shown that humic acids have a specific effect on the processes of structure formation in gelatin-based polymer hydrogels, which is due to the different nature and characteristics of humic substances: the degree of metamorphism of the source coal, volatile matter and oxygen content. It was also found that humic substances are active antibacterial agents in the hydrogel, which slow down the formation of mold in them. Therefore, it is promising to obtain hybrid environmentally friendly biodegradable polymer films with bactericidal properties using hybrid modifiers - humic substances.

The purpose of this article is to investigate the features of the influence of humic substances on the processes of structure formation of hydroxypropyl methylcellulose solutions to obtain hybrid environmentally friendly biodegradable polymer films.

2. Experimental part

2.1. Raw materials

In the study, as a polymer base for the manufacture of hydroxypropyl methylcellulose brand Walocel™ MT 400 PFV, manufactured by Dow Corning, USA. Hydroxypropyl methylcellulose (Fig. 1) is a natural water-soluble polymer. The physical properties of hydroxypropyl methylcellulose are given in Table 1. This substance dissolves easily and quickly in hot or cold water, forms solutions with different levels of viscosity.

As a catalyst for crosslinking of hybrid environmentally friendly biodegradable polymer films, citric acid (99.88%) according to GOST 3652 [19] is used. To obtain humic substances used coal of low degree of metamorphism, the characteristics of which are given in Tables 2-3.

Table 1.Physico-chemical properties of hydroxyethylcellulose

Characteristic	Value
Solubility	water soluble, delayed solubility in pH neutral cold water
Moisture content	7%
Color	White
pH solution 1 %	6.4

Table 2. Proximate analysis of coal

Sample	Proximate analysis, % mas			
	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 3. Ultimate analysis 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

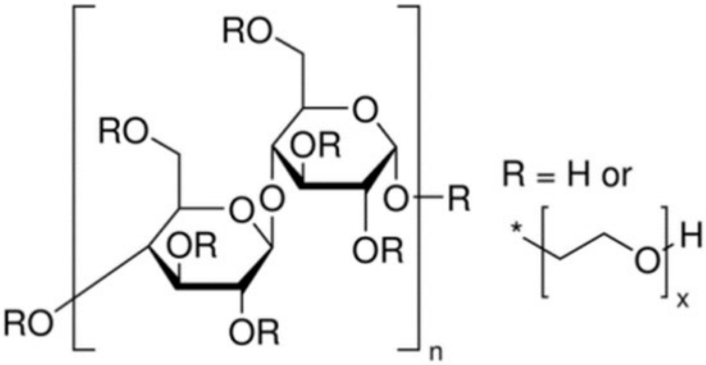


Fig. 1. Structural formula of hydroxyethyl cellulose

2.2. Experimental techniques

Humic acid was obtained according to [20]. The essence of the method consists in processing an analytical lignite 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 hydroxypropyl methylcellulose at a concentration of 2 wt% was obtained by dissolving the polymer in a mass ratio of 2:100 hydroxypropyl methylcellulose: distilled water when heated to 90-100 °C. After that we added to the obtained solutions of hydroxypropyl methylcellulose 1.5% of the mass crosslinking catalyst - citric acid. For the analysis of rheological properties were obtained solutions of hydroxypropyl methylcellulose at different concentrations of humic substances (5, 10, 15% wt.). The samples were stirred at room temperature until complete dissolution of humic substances. Then 50 cm^3 samples were taken from the solutions.

Conductometric studies of hydroxypropyl methylcellulose solutions 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%.

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

The viscosity was determined according to DIN 53211 [21]. 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 [22-24].

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_{ri}). 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_{ijreg}).

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 [23]. The value of mean relative error of approximation was calculated by the formula (1):

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

where n is the amount of sampling (number of experiments), Y_{ij} – values observed during the experiments, Y_{ijreg} – 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:

$$F = \frac{S^2_{reg_i}}{S^2_{res_i}} \tag{2}$$

where $S^2{}_{reg,i}$ is dispersion of experimental response functions relative to their mean values and $S^2{}_{reg,i}$ is residual dispersion of response functions.

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

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

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

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 [22].

3. Results and discussion

The graphical dependence of the conditional viscosity of solutions of hydroxypropyl methylcellulose solutions on the content of different types of humic substances was shown in Fig. 2.

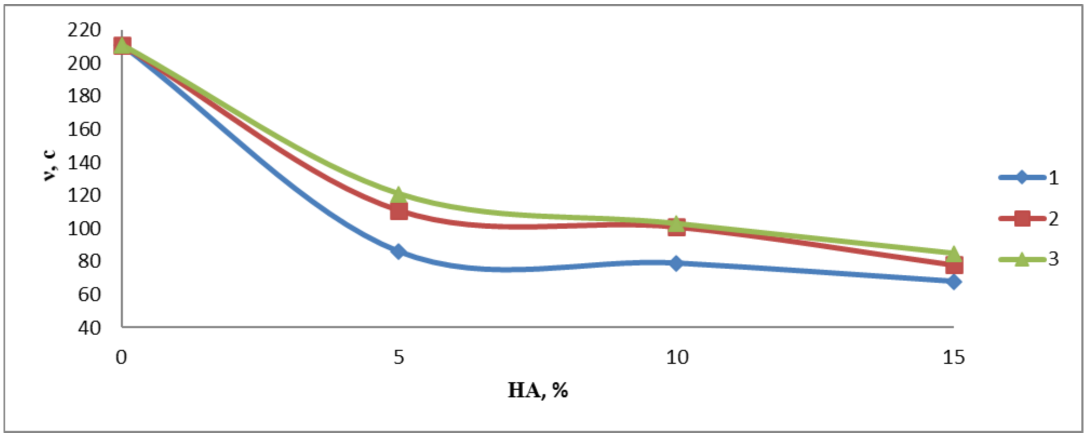


Fig. 2. Graphic dependence of the conditional viscosity of hydroxyethyl cellulose solutions on the content of different types of humic substances

The introduction of all investigated types of humic substances in solutions of hydroxypropyl methylcellulose causes a decrease in its viscosity due to the introduction of an additional amount of solvent, because humic substances are introduced in the form of 8.5% of the mass solutions. The effect of the solvent of humic substances increases in a number of HA1>HA3>HA3.

Next, the processes of structure formation by the method of conductometry were studied, the results of which are presented in Fig. 3-5 in the form of graphical dependences of specific electrical conductivity of hydroxypropyl methylcellulose solutions on the content of different types of humic substances.

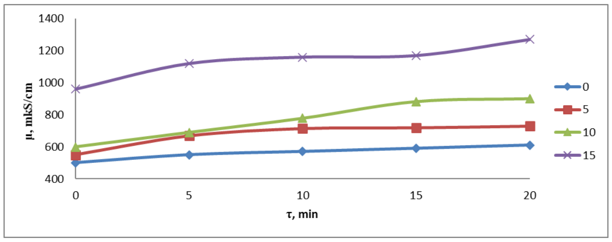


Fig. 3 Dependence of specific conductivity of hydroxyethyl cellulose solutions on the content of humic acid obtained from sample №1

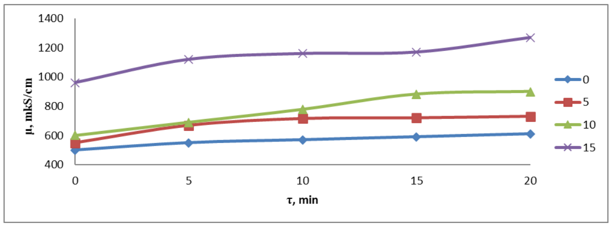


Fig. 4 Dependence of specific conductivity of hydroxyethyl cellulose solutions on the content of humic acid obtained from sample № 2

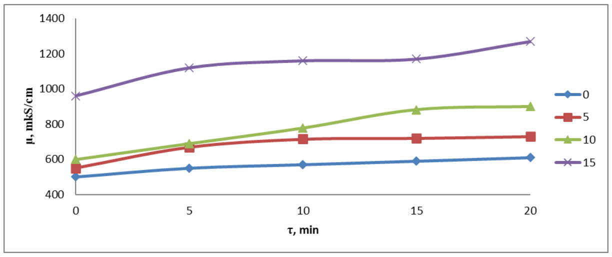
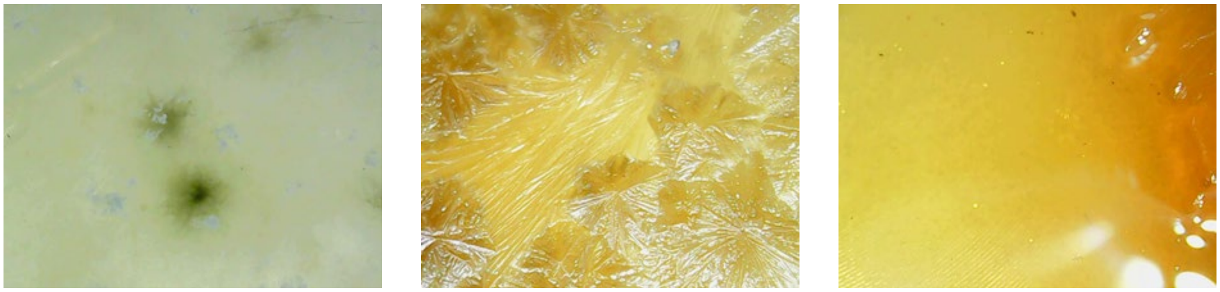


Fig. 5 Dependence of specific conductivity of hydroxyethyl cellulose solutions on the content of humic acid obtained from sample № 3

Fig. 6. Pure hydroxyethyl cellulose solution

The introduction of humic hydroxypropyl methylcellulose solutions causes an increase in the intensity of structure formation processes, which leads to an increase in the specific electrical conductivity of hydroxypropyl methylcellulose solutions with an increase in the content of different types of humic substances. The effect of strengthening the structure is different depending on the properties of humic substances and increases in a number of HA3>HA2>HA1. This pattern is confirmed by the data of microscopic studies, the results of which are presented in Figs. 6-9.

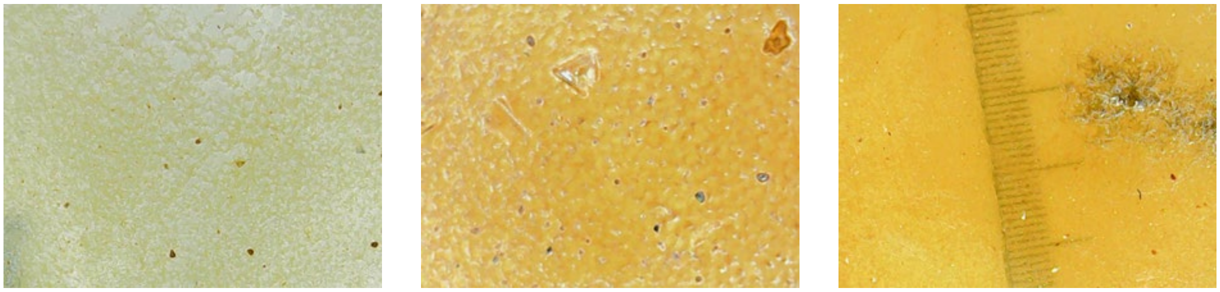


5%HA1 10%HA1 15%HA1

Fig.7. Photographs of solutions with humic acids from sample 1

5%HA2 10%HA2 15%HA2

Fig.8. Photographs of solutions with humic acids from sample 2



5%HA3 10%HA3 15%HA3

Fig.9. Photographs of solutions with humic acids from sample 3

From microphotographs it is clear that with increasing content of humic substances in the studied solutions of hydroxypropyl methylcellulose there is a greater agglomeration of the polymer, which indicates an increase in the processes of structure formation in them. The effect of strengthening the agglomeration processes in the studied samples of hydroxypropyl methylcellulose solutions is different depending on the properties of humic substances and increases in a similar for the formation of the series HA3>HA2>HA1.

Based on the experimental data shown in Fig. 2-6, a linear mathematical model has been established in response to the process of characteristics of a specific system (experimental-statistical mathematical models, ESMM), which are presented in table 4, 5.

The average relative errors ε indicate that the correspondence of the constructed models to the experimental data can be considered good (ε = 10-20% - the accuracy of the forecast is good [23]). Tabular critical values of Fisher's criterion at the level of significance α=0.05: for conditional viscosity F_{1cr}=2.91; for conductivity F_{2cr}=1.39 and are less than the calculated values given in Tables 4, 5. Therefore, the obtained data indicate the adequacy of the developed linear ESMM.

Table 4. ESMM dependence of conditional viscosity of hydroxypropyl methylcellulose solutions on process factors and characteristics of coal

No.	Equation type	Assessment of statistical significance and adequacy			
		R^2	R	ε, %	F
1	$\nu_1 = 174.0477 - 8.2733 \cdot HA + 0.1808 \cdot V^d$	0.7542	0.8685	20.92	3.36
2	$\nu_2 = 251.4615 - 8.2733 \cdot HA - 0.96348 \cdot C^{daf}$	0.7764	0.8811	19.30	4.47
3	$\nu_3 = 161.6851 - 8.2733 \cdot HA + 1.0501 \cdot O_d^{daf}$	0.7767	0.8813	19.32	4.48

Table 5. ESMM dependence of conductivity of hydroxypropyl methylcellulose solutions on process factors and characteristics of coal

No.	Equation type	Assessment of statistical significance and adequacy			
		R^2	R	ε, %	F
4	$\mu_1 = 441.06 + 6.112 \cdot HA + 29.98 \cdot \tau - 1.11622E - 16 \cdot V^d$	0.8659	0.9305	17.35	1.47
5	$\mu_2 = 441.06 + 6.112 \cdot HA + 29.98 \cdot \tau + 8.3608E - 16 \cdot C^{daf}$	0.8659	0.9305		
6	$\mu_3 = 441.06 + 6.112 \cdot HA + 29.98 \cdot \tau - 2.96237E - 16 \cdot O_d^{daf}$	0.8659	0.9305		

4. Conclusions

The peculiarities of the influence of humic substances on the processes of structure formation of hydroxypropyl methylcellulose solutions for obtaining hybrid ecologically pure biodegradable polymer films were investigated.

The modifying effect of humic substances, which were obtained from three different samples of low-grade Ukrainian coal, was studied. Hydroxypropyl methylcellulose solutions modified with humic substances of various origins were obtained to obtain ecologically pure biodegradable polymer films on their basis.

A study of the influence of humic substances on the processes of structure formation in solutions of hydroxypropyl methylcellulose , on the basis of which it was shown that they are due to the different nature and characteristics of humic substances.

Symbols

W^a – moisture contents, %;
A^d – ash content, %;
V^d – volatile matter, %;
C^d – content of carbon, %;
H^d – content of hydrogen, %;
N^d – content of nitrogen, %;
S^d_t – content of sulfur, %;
O^d – content of oxygen, %;
v – conditional viscosity, s;
μ – conductivity, mkS/cm;
R^2 – the coefficient of determination, %;
R – the coefficient of regression;
ε – the mean relative error of approximation, %;
F – Fisher criterion;
HA – humic acid, %
τ – time of reaction, min.

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