

**THE USE OF HUMIC ACIDS FROM LOW-GRADE METAMORPHISM  
COAL FOR THE MODIFICATION OF BIOFILMS BASED ON POLYVINYL  
ALCOHOL**

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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.

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.

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 [1].

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

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). Ehe 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.

For our researches we used polyvinyl alcohol (Kuraray, Japan) of the "Mowirol 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 the work.

Humic acid was obtained according to [2]. 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<sup>3</sup> 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 mks/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 [3]. 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<sup>3</sup> of the test material through a calibrated nozzle with 4 mm diameter of a VZ-246 viscometer at a certain temperature.

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 [4–6].

The estimation of model adequacy is conducted using the following parameters: the mean relative error of approximation ( $\varepsilon_i$ ); 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 ( $Y_{ij}^{reg}$ ).

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 [5].

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

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

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:

$$F = S_{reg\ i}^2 / S_{res\ i}^2 \quad (2)$$

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.

$$S_{res\ i}^2 = \frac{1}{n-1} \sum_{j=1}^n (Y_{ij} - \bar{Y}_i)^2 \quad (3)$$

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

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

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  $\alpha$  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 [4].

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). 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,

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.

Studies have also shown 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.

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.

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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**УДК 662.614.2**

### **ВДОСКОНАЛЕННЯ МЕТОДУ ОЦІНКИ ОКИСНЕННЯ ТА СТУПЕНЯ ОКИСНЕННЯ ВУГІЛЛЯ**

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### **IMPROVEMENT OF THE METHOD OF EVALUATION OF OXIDATION AND THE DEGREE OF OXIDATION OF COAL.**

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Based on the method of determining the oxidation of coal, a method was developed, implemented as a draft national standard and approved in the form of