STUDY OF BROWN COAL HUMIC SUBSTANCES HYBRID MODIFICATION TECHNOLOGY FOR DESIGN BIODEGRADABLE POLYMER MATERIALS

Abstract. The aim of the given work was to study of brown coal humic substances hybrid modification technology for design biodegradable polymer materials. An overview of the current trend in the development, production and application of efficient biodegradable polymer materials and composites is given. The main ways of hybrid modification of biodegradable polymeric composite for obtaining effective products based on them are presented. It is shown that it is promising to obtain biodegradable polymeric materials based on brown coal humic substances hybrid modification technology. Optimization studies have been conducted to determine the most effective composition of biodegradable polymeric materials based on bioplastics polylactide and coffee waste modified with humic substances. It was found that filling the bioplastic polylactide with such coffee waste as coffee husk is more effective as with coffee grounds. It was found that the optimal content is 60% wt. coffee husk, that was modified by humic substances (2% wt.).
Keywords: brown coal, humic substances, hybrid, modification, technology, biodegradable, polymer, materials.

Statement of the problem. Nowadays, the concept of Zero Waste, which is connected with the appearance of various biodegradable polymers that are supposed to replace traditional non-biodegradable plastics, has actually become a modern trend of humanity [1, 2]. At the same time, is perspective to keep biodegradable polymeric materials modified with inorganic and organic nature reagents [3, 4, 5].

In general, carbon and carbon materials are now known as immobilized or included in the polymer matrix hybrid modifiers, which allow to produce effective sorbent, ion exchange and antimicrobial materials for various industries: electronics, medicine, instrumentation and others. That is why it is perspective to make hybrid biodegradable polymeric materials modified with humic substances with two virtually opposite characteristics - bioresistance to microorganisms and the ability to biodegrade. There are significant deposits of lignite and low-metamorphosed coal in the world (including Ukraine).

Analysis of recent research and publications. Currently, lignite has very limited use due to poor technological characteristics (high ash content, moisture and sulfur content). It is proposed to use lignite in the oxidative desulfurization process [6], to produce boiler fuel components or bitumen [7, 8] and in gasification processes [9].

However, the lignite application direction seems to be the most perspective for the humic acids and subsequent production of polymeric materials. In our previous work [10], polymer hydrogels 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 source coal metamorphism, volatile matter yield and oxygen content. It was also found that humic substances are active antibacterial agents in the hydrogel, which slow down the mold formation in them [11]. Therefore, it is perspective to design effective brown coal humic substances hybrid modification technology for biodegradable polymer materials.

The article aims. The work’s aim was to study of brown coal humic substances hybrid modification technology for design biodegradable polymer materials.

To achieve this aim in the work it was necessary to perform the following tasks:

- to study the coffee grounds and husk wastes and modifications with humic substances impact on the biodegradable polymeric materials physical and mechanical properties complex;
- to determine the optimal content and type of coffee grounds and husks in the polylactide to obtain highly effective biodegradable polymeric materials.

**Raw materials and test methods.** The objects of study were:

- plastic bland of polylactide Terramac TP–4000;
- coffee grounds and husk with polyfractional composition in the particle size limit from 0.5 to 1 mm.
- humic substances was obtained according to ISO 5073. To obtain humic substances used coal of low degree of metamorphism, the characteristics of which are given in table 1.

**Table 1**

<table>
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<tr>
<th>Proximate and ultimate analysis of brown coal*</th>
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<td>Proximate analysis, % mas</td>
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<tr>
<td><strong>W</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>16.8</td>
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<tr>
<td>Ultimate analysis, % mas</td>
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<tr>
<td><strong>C</strong>&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>80.83</td>
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*W<sup>a</sup> – moisture contents, %; A<sup>d</sup> – ash content, %; V<sup>d</sup> – volatile matter, %; C<sup>d</sup> – content of carbon, %; H<sup>d</sup> – content of hydrogen, %; N<sub>daf</sub> – content of nitrogen, %; S<sub>t</sub> – content of sulfur, %; O<sub>d</sub> – content of oxygen, %

Composites were obtained by extruding pre-prepared raw materials in a single-screw laboratory extruder at a temperature of 170–200 °C and a roll rotation speed of 30–100 rpm.

The study of impact strength and breaking stress during bending of the samples without notching at a temperature of 20 °C was carried out on a pendulum head according to ISO 180 and ISO 178, respectively.

Specific surface to an accuracy of ±10 % was measured by the BET method of BETH (Brownauer, Emmett and Teller) by the adsorption of gaseous nitrogen at temperature 196 °C. The samples were prepared by degassing for one hour at room temperature (25–30 °C) and a pressure of 0.01 mm Hg Art. Weighing of samples was carried out with to accuracy of 0.00001 g.

Potentiometric study of aqueous suspensions of fillers by the method of A. P. Nechyporenko [12] was carried out at room temperature (20–25 °C) using the portable pH-meter PH-200 Waterproof Professional Series pH/Temp Meter (USA) with an accuracy of measuring the hydrogen index of ±0.001 pH. In accordance with the procedure, we studied the pattern of change in the values of pH<sub>susp</sub>. over time τ. We added 10 cm<sup>3</sup> of distilled boiled water with pH<sub>0</sub>=6.8–7.0 to the potentiometric cell with a glass and silver chloride electrodes.
After stabilization of the potential of glass electrode (in 2–3 minutes at continuous agitation with a magnetic stirrer), we added a batch of the filler with a weight of (~0.2 g). We started a stopwatch simultaneously. Measurement of pHsusp. was performed every 5 seconds over the first minute of contact between the filler and water and after each minute over the following 5 minutes. By the position of extrema on the constructed graph of dependence pHsusp.=f(τ) we assessed the instantaneous surface reaction, which indicates the type of active centers that dominate on the surface. Using the graph, we also determined the value of pHsusp in the state of chemical equilibrium.

**Results and discussion.** The initial step of our study of brown coal humic substances hybrid modification technology for design biodegradable polymer materials was to determine the type and coffee grounds and husks content impact on the physical and mechanical properties level for polylactide: impact strength and tensile stress during bending - Fig. 1-2

![Graph](image-url)
Fig. 2. Coffee grounds content impact on the physical and mechanical properties level for biodegradable polymeric materials based on polylactide

Fig. 1-2 shows the opposite effect of filling with coffee grounds and husks on the physical and mechanical properties level for biodegradable polymeric materials: the introduction of coffee husks leads to their reduction, and coffee ground - vice versa. In our opinion, this fact is due to the different affinity of the acid-reducing properties of coffee husks and coffee grounds surfaces with polylactide - Fig. 3.

Fig. 3. Dependences of change in aqueous suspensions pH from the contact time between coffee grounds, coffee husk, polylactide and water
Figure 3 shows that the coffee husk surface is characterized by the weakly acidic active centers, while the coffee grounds surface can be noted the active centers of a neutral nature. It should also be noted that the filling of polylactide with coffee grounds allows to increase almost 1.5 times the impact strength and the breaking stress during bending level for biodegradable polymeric materials, with the maximum value is typical for 50% of the filling.

Next, the brown coal humic substances hybrid modification technology effect on the physical and mechanical properties for biodegradable polymeric materials with the optimal coffee husk content (50% wt) was studied - Fig. 4:

![Graph showing impact strength and breaking stress during bending vs. humic substances content]

**Fig. 4.** Impact of brown coal humic substances hybrid modification technology by humic substances content on the physical and mechanical properties level for biodegradable polymeric materials based on polylactide with 50% coffee husk content

Fig. 4 shows that the brown coal humic substances hybrid modification technology with humic substances (2% wt) can increase the physical and mechanical properties complex for biodegradable polymeric materials. The increase in the physical and mechanical properties for biodegradable polymeric materials when modified with humic substances is associated with a decrease in the total specific surface area from 7.3 m$^2$/g to 3.5 m$^2$/g, which indicates that the introduction of humic substances increases the polymer material homogeneity in general.

**Conclusion.** Optimization studies have been conducted to determine the most effective composition of biodegradable polymeric materials based on polylactide and coffee waste in the form of husks and coffee grounds by brown coal humic
substances hybrid modification technology. It was found that filling the polylactide with coffee waste in the form of coffee grounds is more effective compared to coffee husks. It was found that in brown coal humic substances hybrid modification technology the optimal coffee grounds content is 50% wt. It is also shown that the brown coal humic substances hybrid modification technology with optimal humic substances content 2% wt. allows to increase the physical and mechanical properties complex for biodegradable polymeric materials.

References: