

Design and Research of Environmentally Friendly Polymeric Materials Modified by Derivatives of Coal

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Abstract

The aim of the given work was to design new ecologically friendly polymer materials modified by derivatives of coal. An overview of the current trend in the development, production and application of efficient environmentally friendly polymer materials and composites is given. The main ways of hybrid modification of environmentally friendly polymeric composite for obtaining effective products based on them are presented. It is shown that it is promising to obtain environmentally friendly polymeric materials based on coffee waste using hybrid modifiers in the form of humic substances. Optimization studies have been conducted to determine the most effective composition of new environmentally friendly polymeric materials based on bioplastics "OK compost HOME" and coffee waste modified with humic substances. It was found that filling the bioplastic "OK compost HOME" with such coffee waste as coffee husk is more effective as with coffee grounds. It was found that the optimal content is 60 % mass coffee husk, that was modified by humic substances (2 % mass).

Keywords: *Coal; Humic substances; Coffee husk; Polymer; Quality.*

1. Introduction

The modern stage of human development is a high-tech, comfortable and dynamic environment for each of us, which is created thanks to the use of a large number of various polymers and plastics. These are light, bright, durable and easy-to-use materials that due to their ability to take any shape and color, are found everywhere - clothing, packaging, devices, entertainment, sports, transport, medicine and many others. In fact, it can be said that modern man will not be able to fully exist without their use, but at the same time, along with their uniqueness and irreplaceability, polymers and plastics have a significant disadvantages - the generation of a large amount of waste that pollutes the environment and nature around. Because of that, 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, 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 requirements [3-5]. That is why it is perspective 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 [6-8].

An 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 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 environmentally friendly biodegradable polymeric materials modified with humic substances with two virtually opposite characteristics-biore-sistance to microorganisms and the ability to biodegrade. There are significant deposits of lignite and low-metamorphosed coal in the world (including Ukraine).

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 [10-11] and in gasification processes [12-14].

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 [15-16], 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 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 [17]. Therefore, it is perspective to produce hybrid environmentally friendly polymeric materials with bactericidal properties using hybrid modifiers - humic substances.

The work's aim was environmentally friendly polymeric materials modified by derivatives of coal studying and designing.

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 environmentally friendly polymeric materials physical and mechanical properties complex;
- to determine the optimal content and type of coffee grounds and husks in the "OK compost HOME" material to obtain highly effective environmentally friendly polymeric materials.

2. Raw materials and test methods

The objects of study were:

- plastic bland of PBAT, corn starch, PLA «OK compost HOME» brand;
- coffee grounds and husk, gathered in 8 different coffee shops in Kharkiv and dried to instant moisture content. Coffee grounds waste have poly fractional composition in the particle size limit from 0.5 to 1 mm. Using IR spectroscopy methods, it has been shown [18-20] that coffee grounds, in their chemical composition, are characterized by up to 6% or more content of caffeine, alkaloids and their companions, up to 1 % of chlorogenic acids and their derivatives content. The general performance of the peak in the absorption length range from 2900 cm^{-1} to 1800 cm^{-1} indicates the presence of water in the samples.
- humic substances was obtained according to [21]. To obtain humic substances used coal of low degree of metamorphism, the characteristics of which are given in Table 1.

Table 1. Proximate and ultimate analysis of coal*

Proximate analysis, % mas				
W^a	A^d	S_t^d	V^d	
16.8	48.7	2.50	29.1	
Ultimate analysis, % mas				
C^d	H^d	N^{daf}	S_t^d	O_d^d
80.83	4.48	1.29	2.50	10.90

* W^a – moisture content, %; A^d – ash content, %; V^d – volatile matter, %; C^d – content of carbon, %; H^d – content of hydrogen, %; N^d – content of nitrogen, %; S_t^d – content of sulfur, %; O^d – 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 L/D ratio of the extruder is 25, and in order to increase the uniformity of dispersed waste distribution in the finish compositions, 2 mass passes were used to obtain finished samples.

It was made 20 parallel experiments for each composition, statistical processing was made by characteristics such as arithmetic mean, standard deviation and variation coefficient.

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 $\pm 10\%$ was measured by the BET method by the adsorption of gaseous nitrogen at temperature 196°C. Microscopic studies were carried out using the electron microscope Digital Microscope HDcolor CMOS Sensor (China).

Potentiometric study of aqueous suspensions of fillers by the method of A. P. Nechyporenko [22] 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.

3. Results and discussion

The initial step of our study was to determine the type and coffee grounds and husks content impact on the physical and mechanical properties level for environmentally friendly polymeric materials: impact strength and tensile stress during bending - Figs. 1-2.

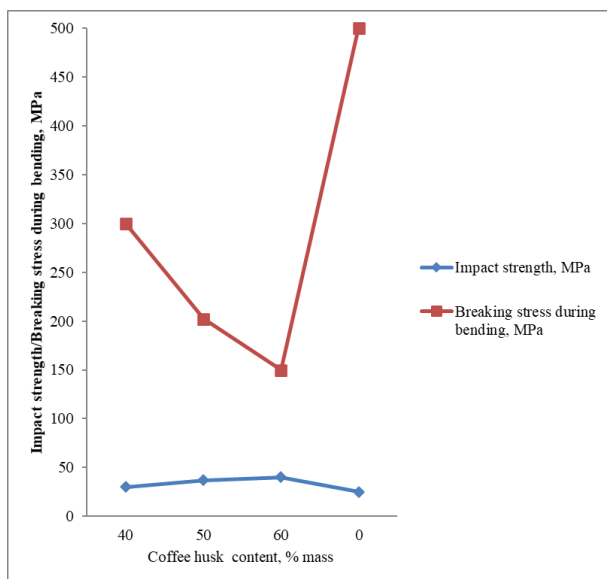


Fig. 1 Coffee husk content impact on the physical and mechanical properties level for environmentally friendly polymeric materials based on "OK compost HOME" plastic

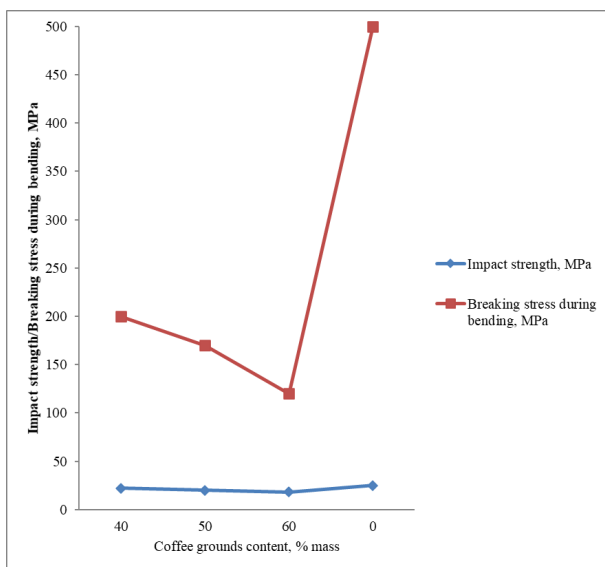


Fig. 2. Coffee grounds content impact on the physical and mechanical properties level for environmentally friendly polymeric materials based on "OK compost HOME" plastic

Figs. 1-2 shows the opposite effect of filling with coffee grounds and husks on the physical and mechanical properties level for environmentally friendly polymeric materials: the introduction of coffee grounds leads to their reduction, and coffee husks - 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 "OK compost HOME" plastic - Fig. 3.

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 "OK compost HOME" plastics with coffee husks allows to increase almost 1.5 times the impact strength level for environmentally friendly polymeric materials, with the maximum value is typical for 60 % mass of the filling.

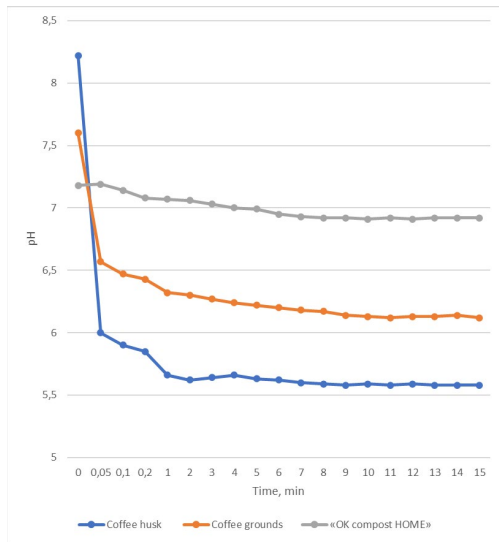


Fig. 3 Dependences of change in aqueous suspensions pH from the contact time between coffee grounds, coffee husk, «OK compost HOME» plastic and water

At the same time, the breaking stress during bending when filling, both coffee husks and coffee grounds is reduced. The latter fact suggests that both of the studied coffee wastes lead to increased stiffness and reduced elasticity of environmentally friendly polymeric materials.

Below in Fig. 4 shows surface's photomicrographs of new environmentally friendly polymeric materials based on "OK compost HOME" plastic. Next, the modification effect using humic substances on the physical and mechanical properties for environmentally friendly polymeric materials with the optimal coffee husk content (60 % mass) was studied - Fig. 5.

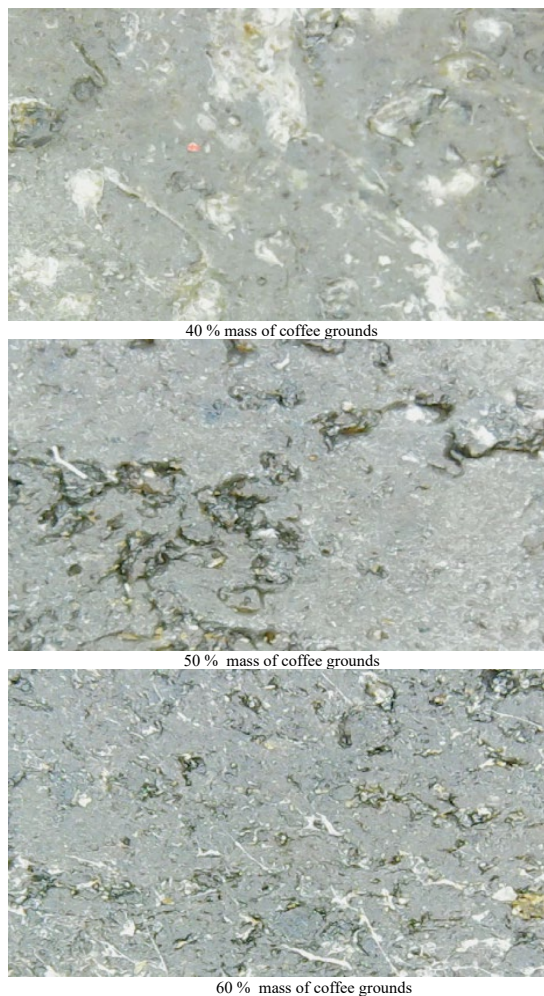


Fig. 4. Surface's micrographs of new environmentally friendly polymeric materials based on "OK compost HOME" plastic with different coffee grounds waste content

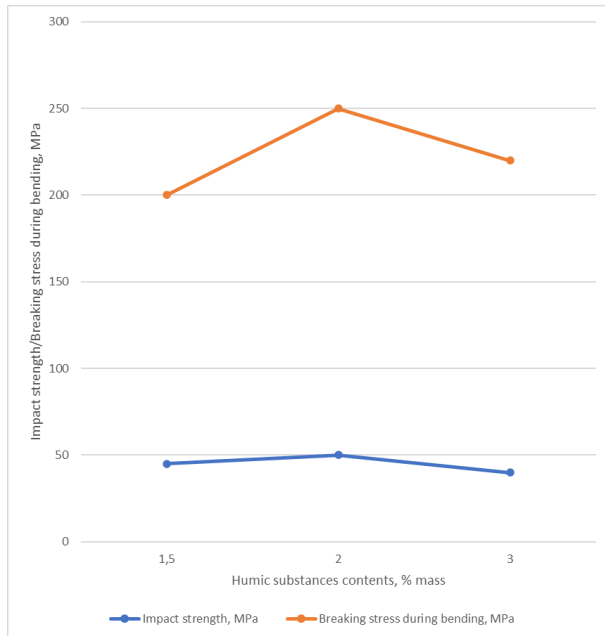


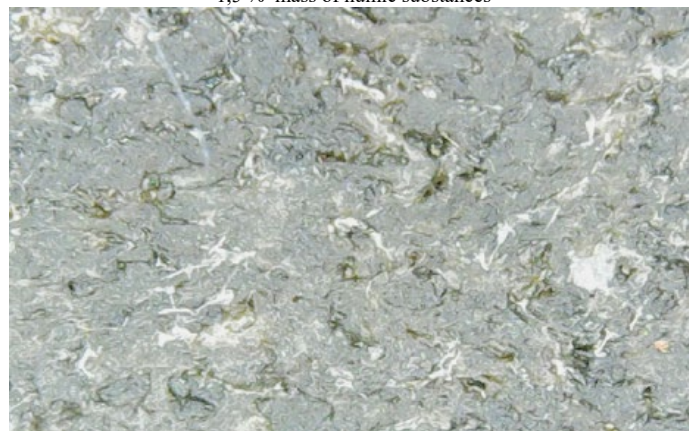
Fig. 5. Impact of humic substances content on the physical and mechanical properties level for environmentally friendly polymeric materials based on "OK compost HOME" plastic with 60% mass coffee husk content

Fig. 5 shows that the modification with humic substances (2 % mass) can increase the physical and mechanical properties complex for environmentally friendly polymeric materials. Below in Fig. 6 shows surface's photomicrographs of new environmentally friendly polymeric materials based on bioplastics "OK compost HOME" and coffee waste in the form of husks and coffee grounds when modified with humic substances.

The increase in the physical and mechanical properties for environmentally friendly polymeric materials when modified with humic substances is associated with a decrease in the total specific surface area from 6.3 m²/g to 2.5 m²/g, which indicates that the introduction of humic substances increases the polymer material homogeneity in general.



1,5 % mass of humic substances



2 % mass of humic substances



3 % mass of humic substances

Fig. 6. Surface's micrographs of new environmentally friendly polymeric materials based on bioplastics "OK compost HOME" and coffee waste in the form of husks and coffee grounds with different humic substances content

4. Conclusion

Optimization studies have been conducted to determine the most effective composition of new environmentally friendly polymeric materials based on bioplastics "OK compost HOME" and coffee waste in the form of husks and coffee grounds when modified with humic substances. It was found that filling the bioplastic "OK compost HOME" with coffee waste in the form of coffee husk is more effective compared to coffee grounds. It was found that the optimal coffee husk content is 60 % mass. It is also shown that the modification with humic substances (optimal content 2 % mass) allows to increase the physical and mechanical properties complex for environmentally friendly polymeric materials.

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