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HYBRID ECO-FRIENDLY BIODEGRADABLE CONSTRUCTION COMPOSITES MODIFIED WITH HUMIC SUBSTANCES

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Abstract. Obtaining hybrid eco-friendly biodegradable structural composites was considered. The aim of this work was to determining the properties of hybrid eco-friendly biodegradable construction composites modified with humic substances.

Hybrid eco-friendly construction composites were obtained on the basis of bioplastic polylactides with the addition as a filler of coffee grounds with a polyfractional composition within a particle size of 0.5 mm to 1 mm and a hybrid modifier – humic substances from brown coal. Hybrid ecofriendly construction composites were obtained by extrusion of pre-prepared raw materials in a single-screw laboratory extruder at a temperature of 170–200 °C and an auger rotation speed of 30–100 rpm. Investigated impact strength, breaking stress during bending, melt flow index (MFI) and melting temperature of hybrid ecofriendly biodegradable structural composites modified with humic substances.

Optimization studies have been carried out to determine the most effective composition of new ecofriendly structural composites based on bioplastics of polylactides, coffee grounds waste and humic substances of three different types. Researching data together with the data of impact strength, allows us to make assumptions about the possibility of forming a variety of products from structurally composite material, herewith a composition with a coffee content of 50 % by mass. deserves a special attention. The data show an increase the impact strength and the breaking stress during bending a hybrid modification of ecofriendly biodegradable construction composites based on polylactide, coffee grounds waste and humic substances in 2.5 times, with optimal in terms of strength characteristics is the content of coffee grounds at 50 % wt. and 0.5 % by mass humic substances with the highest content of volatile substances and the lowest content of carbon. For such hybrid ecofriendly biodegradable construction composites based on polylactide, coffee grounds waste and humic substances, the MFI is characterized by 3.1 g/10 min. and the processing temperature range is 182–188 °C.

It is shown, that the designed hybrid eco-friendly biodegradable structural composites modified with humic substances can be used in the production of high-strength structures and elements for engineering purposes.

Keywords: structural composites, hybrid eco-friendly biodegradable polymers, humic substances.

Introduction. One of the most popular construction materials today are plastic composites, which, with excellent and useful performance characteristics, unfortunately contribute to the

accumulation of a significant amount of waste based on them. In this regard, a new approach to the development of these materials has been formed in scientific circles: obtaining polymer composites with high and stable performance during the time of their use and then capable of destruction under the influence of environmental factors. That is why the current trend is the use of such ecofriendly 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, and such materials are widely used.

A characteristic feature of the processes of obtaining construction composites based on ecofriendly polymeric materials is the task of optimizing their component composition and set of performance characteristics. In fact, almost always high quality and durability of polymer products and structures due to a set of correct choice of material and selection of the most effective method of processing.

Literature review. One of the most effective ways in the obtaining of structural eco-composites is the obtaining of polylactide compositions filled with various inorganic and organic disperse fillers, and today there are significant amount of researches on the use of coffee grounds as a filler in biopolymer composite materials [1–7]. Bioplastic polymer matrices filled with coffee grounds waste have also been studied in scientific articles [8, 9], but these works are more scientific than applied industrial in nature.

In our previous works [10–12], it was established that the high efficiency of the processes of obtaining eco-friendly biodegradable polymer composite materials based on polylactide and coffee grounds wastes, which are characterized by sufficiently high strength characteristics and resistance to many aggressive environments.

Very relevant are further researches on the design and study of hybrid eco-friendly biodegradable structural composite materials based on polylactide and coffee grounds waste with their combined functional hybrid modification with humic substances (HS), which were studied in previous researches as structuring agents in different types of biopolymers [13, 14]. That is why it is very important to design and optimize effective chemical compositions of hybrid eco-friendly biodegradable structural composite materials based on bioplastics such as polylactide, coffee grounds waste with their combined functional hybrid modification with humic substances to achieve such biodegradable polymeric structural composite materials of optimal complex of operational properties.

The purpose and objectives of the study. The purpose of this work was to study hybrid ecofriendly biodegradable construction composites modified with humic substances.

The objects of study were:

– plastic bland of PLA Terramac TP–4000;

– coffee grounds and husk, gathered in 8 different coffee shops in Kharkiv and dried to instant moisture content 50 %. Coffee grounds waste have poly fractional composition in the particle size limit from 0.5 mm to 1 mm. Using IR spectroscopy methods, it has been shown [10, 11] 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, which were obtained by extraction of brown coal with alkaline solution of sodium pyrophosphate, followed by extraction with 1 % sodium hydroxide solution and precipitation with mineral acid. The essence of the method is to treat an analytical sample of fuel with an alkaline solution of sodium pyrophosphate, followed by extraction of the sample with a solution of sodium hydroxide, precipitation of humic acids with excess mineral acid and determining the mass of the precipitate. Indicators of the quality of used brown coal to obtain humic substances are given in Tables 1–2.

Table 1 – Proximate analysis of coal*

Sample	Proximate analysis, % mas			
	W^a	A^d	S^d_t (S^{daf}_t)	V^{daf} (V^d)
HS1	16.8	48.7	2.08 (2.50)	56.7 (29.1)
HS2	8.1	8.3	1.72 (1.87)	47.7 (43.7)
HS3	30.6	36.7	2.78 (4.00)	63.0 (43.7)

* HS – humic substances, W^a – moisture contents, %; A^d – ash content, %; S^d_t – content of sulfur, %; V^d – volatile matter, %.

Table 2 – Ultimate analysis of coal*

Sample	Ultimate analysis, % mas				
	C^{daf}	H^{daf}	N^{daf}	S^{daf}_t	O^{daf}_d
HS1	80.83	4.48	1.29	2.50	10.90
HS2	68.10	4.57	1.35	1.87	24.11
HS3	60.71	4.87	1.30	4.00	29.12

*C^d – content of carbon, %; H^d – content of hydrogen, %; N^d – content of nitrogen, %; O^d – content of oxygen, %.

Experiment Methodology. Hybrid eco-friendly biodegradable 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.

Investigations of the melt flow index (MFI) were performed using the IIRT-M device at 190 °C and a load of 2.16 kgf.

The melting temperature was determined on a brass disk with a diameter of 50 mm and a thickness of 19 mm with a side hole under the thermometer with a diameter of 9 mm. The brass disk equipped with a thermometer was gradually heated with a gas burner. Samples of polymers with a size of 10×10 mm were placed on it. Temperature intervals of melting and destruction were recorded visually.

Results and discussion. At the initial stage, the optimal content of coffee grounds in hybrid eco-friendly biodegradable structural composites based on polylactide, coffee grounds and humic substances in terms of achieving maximum physical and mechanical properties: impact strength and breaking stress during bending – Fig. 1–2. The influence of coffee grounds content in hybrid modification in systems of humic substances on MFI and melting temperature was also studied – Fig. 3–4.

From Fig. 1 can be seen if we compare the dependence of value of the impact strength of highly filled hybrid systems polylactide – humic substances – coffee grounds on the content of coffee grounds, then there is a tendency to increase the value of the latter with increasing filler content [10]. These data indicate an increase in impact strength for coffee filled humic substances systems of 2.5 times for the sample with a content of 50 %, which is predictable, because filled polymeric materials always have a higher impact strength than homopolymers.

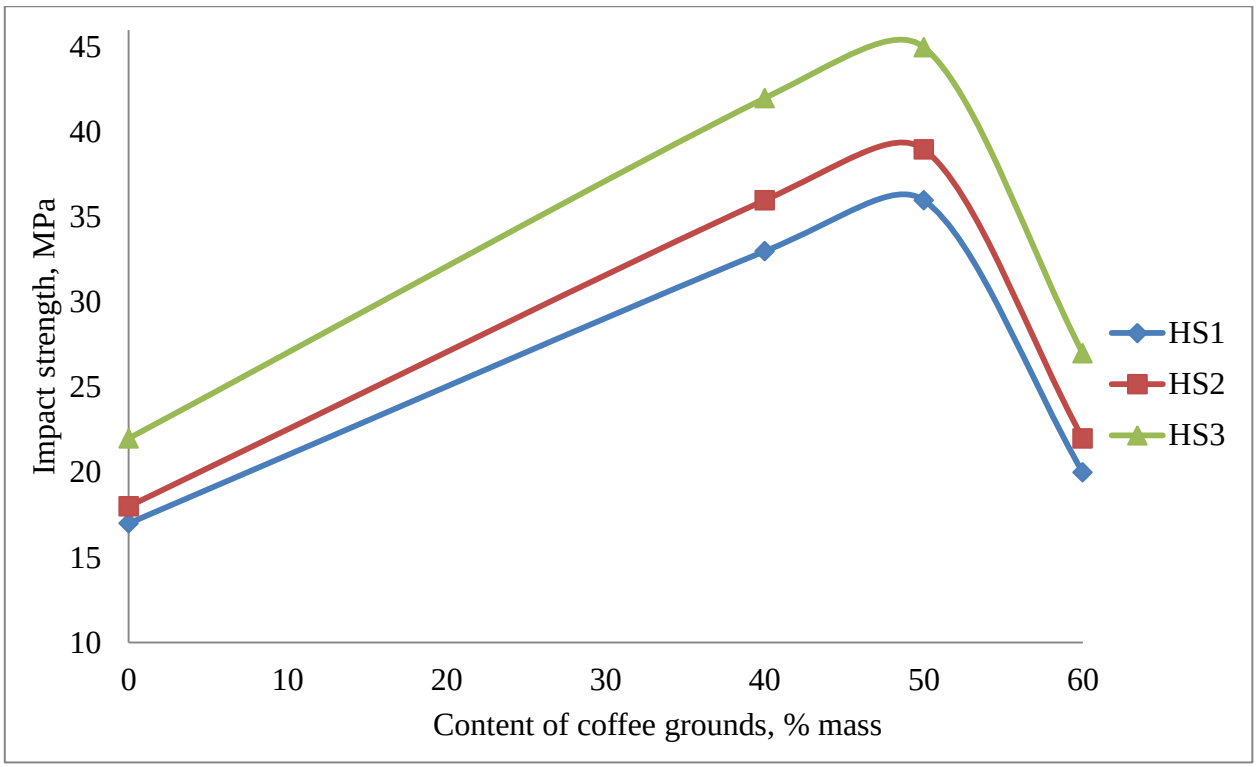

Fig. 1. Dependence of the impact strength of systems of polylactide – humic substances – coffee grounds on the content of coffee grounds

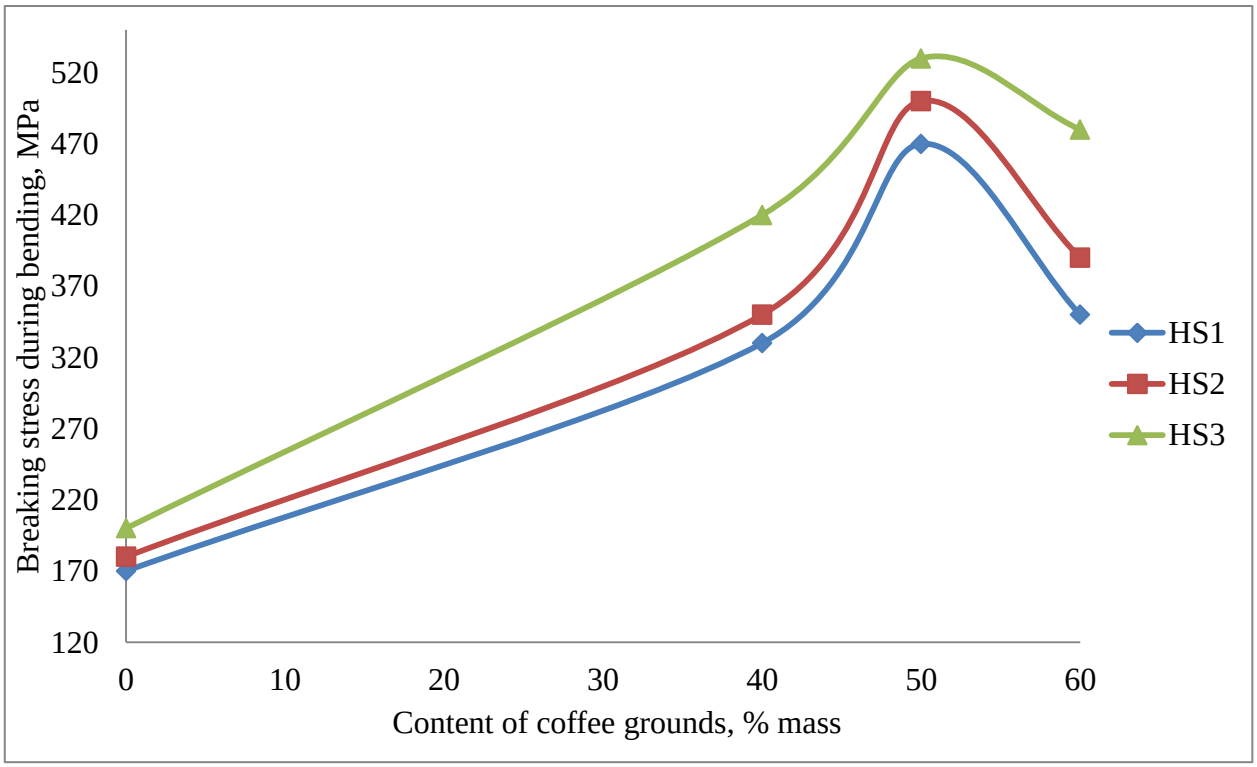

Fig.2. Dependence of the breaking stress during bending of systems of polylactide – humic substances – coffee grounds on the content of coffee grounds

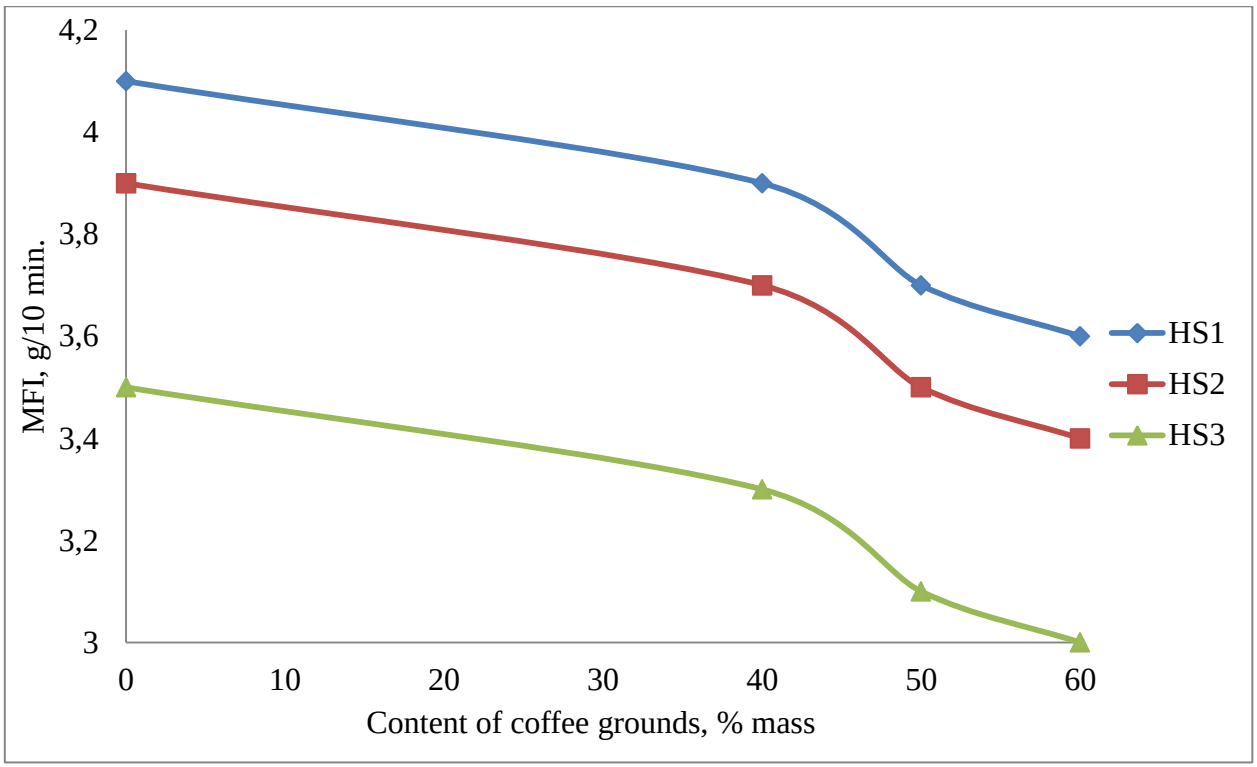

Fig. 3. Dependence of MFI of systems of polylactide – humic substances – coffee grounds on the content of coffee grounds

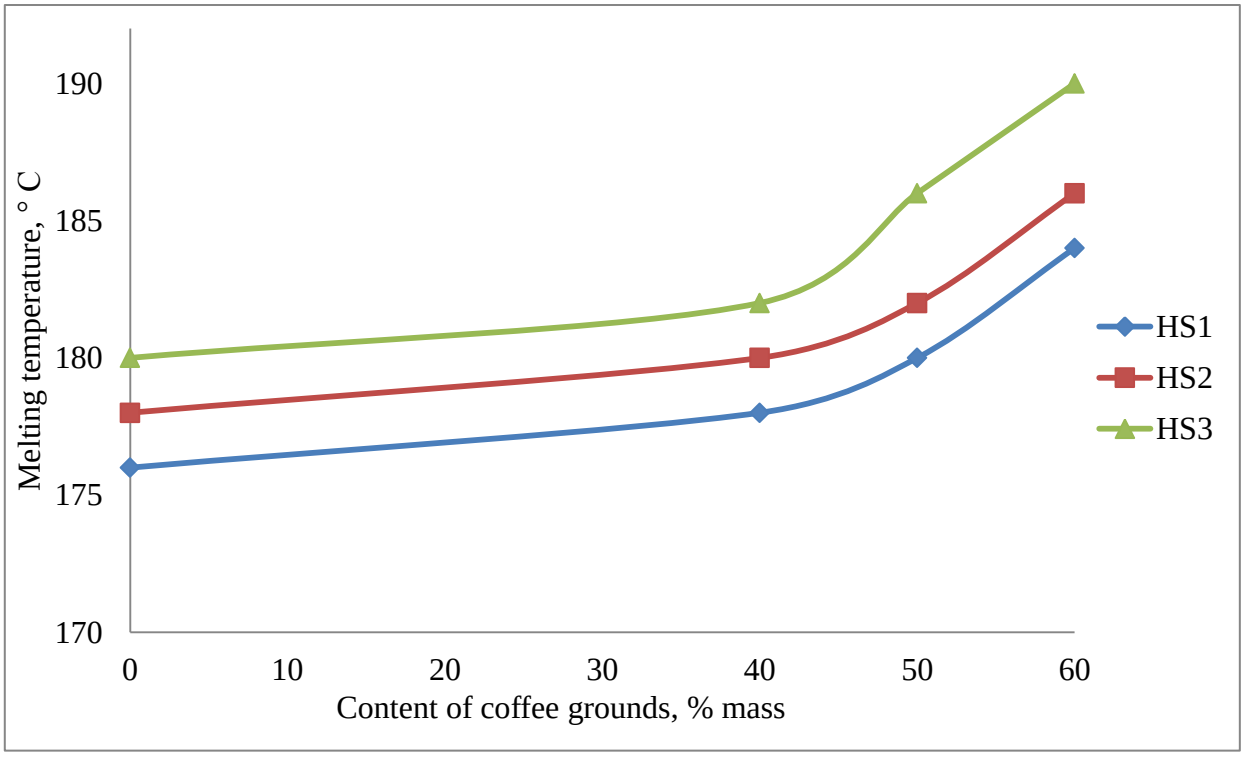

Fig. 4. Dependence of melting temperature of systems of polylactide – humic substances – coffee grounds on the content of coffee grounds

The increase in the value of the breaking stress during bending (Fig. 2) also indicates the processability of hybrid eco-friendly biodegradable structural composites based on polylactide, coffee grounds and humic substances. Thus it becomes obvious that coffee grounds are evenly distributed in the hybrid matrix of polylactide–humic substances [11]. At the same time, it even

slightly "softens" the original rather rigid polylactide. All this, together with the data of impact strength, allows us to make assumptions about the possibility of forming a variety of products from structurally composite material, herewith a composition with a coffee content of 50 % by mass. deserves a special attention. It is also important to clarify that the increase in the complex of physical and mechanical properties of hybrid eco-friendly biodegradable structural composites based on polylactide, coffee grounds and humic substances is related with a decrease in specific surface area from 5.1 m^2/cm to 2.8 m^2/cm, which is indicating that the introduction of coffee grounds increases the homogeneity of hybrid systems of polylactide – humic substances – coffee grounds. Figures 3-4 show that in the hybrid modification there is a decrease in MFI and increase in the melting temperature of the systems polylactide – humic substances – coffee grounds with increasing content of coffee grounds.

Table 3 shows the summary data on physic–mechanical and technological properties of the designed hybrid eco-friendly biodegradable construction composites based on polylactide, coffee grounds waste and humic substances of three different types.

Table 3 – Summary properties on physical-mechanical and technological properties of the designed hybrid eco-friendly biodegradable construction composites based on polylactide, coffee grounds waste and humic substances *

PLA content, % wt.	CG waste content, % wt.	Type of HS at their content of 0.5 % by mass	Impact strength, MPa	Breaking stress during bending, MPa	MFI, g/10 min	Melting temperature, °C
60	40	HS№1	33	330	3.9	178
50	50		36	470	3.7	180
40	60		20	350	3.6	184
60	40	HS№2	36	350	3.7	180
50	50		39	500	3.5	182
40	60		22	390	3.4	186
60	40	HS№3	42	420	3.3	182
50	50		45	530	3.1	186
40	60		27	480	3.0	190

*PLA – polylactide, CG – coffee grounds, HS – humic substances

The data show an increase the impact strength and the breaking stress during bending a hybrid modification of eco-friendly biodegradable construction composites based on polylactide, coffee grounds waste and humic substances in 2.5 times, with optimal in terms of strength characteristics is the content of coffee grounds at 50 % wt. and 0.5 % by mass humic substances №3. For such hybrid eco-friendly biodegradable filled composites based on polylactide, coffee grounds waste and humic substances, the MFI is characterized by 3.1 g/10 min and the processing temperature range is 182–188 °C.

Conclusions. As a result of the performed researches hybrid eco-friendly biodegradable structural composites modified with humic substances were designed. It is established that there is an increase of impact strength and breaking stress during bending of the hybrid modification of eco-friendly biodegradable structural composites based on polylactide, coffee grounds and humic substances in 2.5 times, with optimal in terms of strength characteristics is the content of coffee grounds equal to 50 % by mass. and 0.5 % by mass. of humic substances. Designed hybrid eco-friendly biodegradable structural composites modified with humic substances can be used to obtain high-strength structures and elements of engineering and technical purposes.

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ГІБРИДНІ ЕКОЛОГІЧНО ЧИСТІ БІОДЕГРАДАБЕЛЬНІ КОНСТРУКЦІЙНІ КОМПОЗИТИ, МОДИФІКОВАНІ ГУМІНОВИМИ РЕЧОВИНАМИ

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Анотація. Розглянуто одержання гібридних екологічно чистих біодеградабельних конструкційних композитів. Метою даної роботи було визначення властивостей гібридних екологічно чистих біодеградабельних будівельних композитів, модифікованих гуміновими речовинами.

Отримані гібридні екологічно чисті конструкційні композити на основі біополімеру полілактиду з додаванням в якості наповнювача кавової гущі, висушеної до 50 % вологості з поліфракційним складом з розміром частинок від 0,5 мм до 1 мм та гібридним модифікатором – гуміновими речовинами бурого вугілля. Гібридні екологічно чисті конструкційні композити отримані шляхом екструзії попередньо підготовленої сировини в одношнековому лабораторному екструдері при температурі 170–200 °С та швидкості обертання шнека 30–100 об/хв. В гібридних екологічно чистих біодеградабельних конструкційних композиціях модифікованих гуміновими речовинами досліджували ударну в’язкість, руйнівну напругу при вигині, показник плинності розтопу та температуру топлення.

Проведені оптимізаційні дослідження для визначення найбільш ефективного складу новітніх екологічно чистих конструкційних композитів на основі біополімеру полілактиду, відходів кавової гущі та гумінових речовин трьох різних типів. Отримані дані свідчать про підвищення ударної міцності та розривної напруги при згинанні при гібридної модифікації екологічно чистих біодеградабельних конструкційних композитів на основі полілактиду, відходів кавової гущі та гумінових речовин у 2,5 рази, при оптимальному за міцністю характеристик вмісту кавової гущі 50 % мас. та 0,5 % за масою гумінових речовин з найбільшим вмістом летких речовин та найменшим вмістом вуглецю. Для таких гібридних екологічно чистих біодеградабельних конструкційні композитів на основі полілактиду, відходів кавової гущі та гумінових речовин показник плинності розтопу характеризується значенням 3,1 г/10 хв. і діапазон температур обробки сягає 182–188 °С.

Показано, що розроблені гібридні екологічно чисті біодеградабельні конструкційні композити модифіковані гуміновими речовинами можуть бути використані при отриманні високоміцних конструкцій та елементів інженерно-технічного призначення.

Ключові слова: конструкційні композити, гібридні екологічно чисті біодеградабельні полімери, гумінові речовини.

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