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Polyamide-Polylactide-Humic Substances Biocomposites Hybrid Modification Sustainable Development Technology

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Abstract

In this article, new hybrid biocomposites based on polyamide, PLA and humic substances were developed and studied. The legal regulation peculiarities to ensuring environmental industrial enterprises' safety through the development of biocomposites technologies in Ukraine are considered. It has been established that humic substances, which were obtained from brown coals by extraction method, are characterized by nanodispersion in the range of 52-380 nm. It was found that due to the presence of a large number of active functional groups on the surface of such nanoparticles of humic substances is a hybrid modification of polyamide-polylactide biocomposite by the mechanism of template synthesis, which is accompanied by an increase in the degree of crystallization and the formation of a more rigid polymer structure, which allows to obtain hybrid biopolymer nanocomposites with significant impact strength and breaking stress during bending. It was also found that the obtained hybrid biocomposites based on polyamide- polylactide matrix and humic substances can be used to produce membrane-covering materials for wounds, implants, medical devices and products for dermatological treatment.

Keywords: *Biocomposites; Polyamide; Polylactic acid; Humic substances; Hybrid; Modification; Sustainable development; Legal regulation.*

1. Introduction

An important role in recent years in biopolymeric materials and biocomposites is played by various eco-friendly polymers [1], which in addition to sufficiently high conductive and spectral characteristics, have the ability to biodegrade and implement the principle of «Zero Waste» [2]. Among such eco-friendly materials and composites is polylactide (PLA), which by its chemical nature is an aliphatic thermoplastic polyester made from natural raw materials - corn starch [3]. PLA is a biodegradable plastic obtained by polymerization of lactide dimers with ring opening, and its molecular structure contains mainly L-lactic acid and some isomers of D-lactic acid [4].

According to its properties, PLA is characterized by significant transparency, slow crystallization rate, significant strength properties and manufacturability in relation to various methods of processing into finished products [5-7]. At the same time, one of the most important aspects to be considered in the manufacture of elements and components of different production using biopolymeric materials and biocomposites based on PLA, due to its poor heat resistance and satisfactory mechanical properties [12].

Therefore, mixtures of PLA-based biocomposites with the use of various polymers, organic and inorganic dispersion particles, which allow to increase the mechanical properties and provide specific characteristics by controlling their distribution in the structure of the mixture, have become widespread. The use of organic and inorganic nanoparticles can also further improve and stabilize the structure of PLA-based biomaterials and biocomposites [13-14]. Perspective in this regard is the creation of biocomposites based on PLA and other polymer matrix, hybrid modified with carbon materials in the form of humic substances of brown coal.

Nowadays, the most important tasks in area sustainable development of biocomposites is modern ecologically safe technological processes implementation. This will contribute to ensuring citizens right to a natural environment that is safe for life and health [15-20].

The Ukrainian legislation is aimed at citizens environmental rights ensuring, including the right to a natural environment that is safe for life and health. Thus, among the main environmental protection principles, the Law of Ukraine « On Environmental Protection « (Article 3) enshrines: priority of environmental safety requirements, the obligation to comply with environmental standards and limits on the use of natural resources during economic, management and other activities; greening the material production on the basis of comprehensive solutions in matters of environmental protection, use and restoration of renewable natural resources, the widespread introduction of the latest technologies [21].

According to the Resolution of the Verkhovna Rada of Ukraine No. 188/98-BP dated March 5, 1998 «On the Main Directions of Ukraine State Policy in the Field of Environmental Protection, Use of Natural Resources and Ensuring Environmental Safety» [22], the chemical industry is one of the main industries where large waste volumes are produced, a significant amount of which is toxic.

The main principles (strategy) of Ukraine state environmental policy for the period until 2030 [22] provide the global Sustainable Development Goals by 2030 (SDGs) achievement, which were approved at the United Nations Sustainable Development Summit in 2015 [23]. Thus, among the global Sustainable Development Goals, goal 12 - «responsible consumption and production» is not the last place.

Legal, organizational, and economic principles of activities related to the formation and reduction prevention of waste generation volume, negative consequences reduction from waste management activities, preparation promotion of waste for reuse, recycling and recovery in order to prevent their negative impact on human health and the surrounding natural environment defines the Law of Ukraine «On Waste Management» and other normative legal acts [24]. The goal of the Waste Management Program for 2013-2020 is to implement measures to reduce the waste generation volume, its collection, transportation, storage, processing, utilization, removal, disposal and burial in order to prevent negative effects on the environment and man's health, as well as new technologies introduction [25]. The goal of the National Waste Management Strategy in Ukraine until 2030 is to create conditions for population living standards raising by implementing a systemic approach to waste management at the state and regional level, reducing the waste generation and increasing their processing and reuse [26].

In the European Union, the general requirements and regulations governing waste management are contained in: Directive 2008/98/EU on waste and repealing certain Directives [27]. On December 1, 2022, the Verkhovna Rada of Ukraine adopted the European integration draft of the Law of Ukraine «On Chemical Safety and Management of Chemical Products» (draft law No. 8037) [28]. Article 83 of this Law provides the Unified Center establishment for the international agreements implementation of Ukraine, which regulate waste and chemical products management, and establishes its main tasks.

The Ministry of Environmental Protection and Natural Resources of Ukraine [29] coordinates activities to ensure the fulfillment of Ukraine's obligations arising from its membership in international treaties that regulate issues of waste and chemical product management through the Unified Center for Ensuring the Fulfillment of International Treaties of Ukraine, regulating waste and chemical products management, the provisions of which are approved by the Ministry of Environment of Ukraine.

Central and local bodies of executive power submit to the Unified Center for the Implementation of International Agreements of Ukraine, which regulate waste and chemical products management, the information materials necessary for the tasks performance assigned to it.

In 2017, Ukraine undertook within the framework of the Association Agreement with the EU [30] to implement Directive 2010/75/EU of the European Parliament and of the Council dated November 24, 2010 on industrial emissions (comprehensive pollution prevention and control) [31]. The Directive and the best available technologies application concept determine the procedure for issuing permits for pollutants emission, the maximum permissible volumes of pollution and the list of the best available technologies and management methods for each industry sector and activity type.

Having considered issues complex related to the challenges and threats to the national security of Ukraine in the environmental sphere, the National Security and Defense Council of Ukraine, among other things, instructed the Cabinet of Ministers of Ukraine to develop and approve the National Action Plan for Environmental Protection for 2021-2025 [32], which provides for the creation of databases containing information on the best available methods of industrial and agricultural production and technologies aimed at minimizing environmental pollution, resource and energy conservation, minimizing greenhouse gas emissions, adapting to climate change in all sectors of the economy, using ozone-safe technologies (p. 29) [33].

Today, the Ministry of Environmental Protection and Natural Resources of Ukraine is working on the reform implementation for reduction and control on industrial pollution. On the official website of the Ministry of Environmental Protection and Natural Resources of Ukraine, the Reference Documents on the Best Available Technologies and Management Methods/BREFs translated into Ukrainian are published [34]. Implementation the best available technologies and management methods will allow not only to reduce industrial pollution, negative consequences for the environment and climate, but also to modernize the industry.

It is assumed that the strengthening of environmental protection activities will have positive consequences for citizens and enterprises in Ukraine and the EU, in particular, due to an increase in production level thanks to modern technologies (Chapter 6, Articles 360-366 of the Association Agreement [30]). The strategy for the development of modern industrial coking technologies involves a significant revision of approaches to their implementation in terms of its impact on the environment. It includes stimulating the dirty technologies replacement with ecologically neutral ones, including through a system of environmental protection measures, a repeated increase in the technological processes energy efficiency, the renewable energy sources introduction and resources or waste reuse.

Environmentalization of modern industrial coking technologies is possible in two directions. The first is the comprehensive environmentalization of the entire production, which involves the use of environmentally friendly fuels, technologies, and highly efficient cleaning equipment followed by waste disposal. Direct implementation is usually associated with significant capital expenditures and long implementation times. The second direction involves the management production complex greening by taking into account the environmental factor in its individual structural elements, for example, the secondary raw materials use in the industrial waste form for coking technologies. This, in turn, does not require capital expenditures and is a significant reserve for the enterprises environmental protection activities efficiency.

In our previous works, the functional hybrid effect of humic substances and acids on the structure and properties of a number of biodegradable polymers was proved in order to increase the complex of their operational properties [35-39]. The creation and research of biocomposite materials based on polyamide-PLA matrix for their potential application as biomedical frameworks for the pollutants and heavy metal ions adsorbents production, antibacterial biomaterials, drug delivery systems, sorbents of oil-containing natural, industrial and domestic waters, etc. It has been found [40-41] that heavy metal ions pollution can be reduced by ion exchange, complexation and surface adsorption with the humic substances' participation, while even persistent organic pollutants are first adsorbed and then decomposed by reduction-oxidation processes. The binding of ions in humic substances is special and expands the capabilities of conventional ion exchange resins [42-43]. Perspective in this regard is the creation of biocomposites based on PLA and polyamide matrix, hybrid modified with carbon materials in the form of humic substances of brown coal.

The purpose of the research is to investigate a sustainable development technology of biocomposites hybrid modification by humic substances.

2. Material and methods

2.1. Materials

The objects of the research were: - extrusion PLA of the Terramac TP-4000 brand; - polyamide 6 (Grodnamid PA6-L-211/311). It is the baseline injection moulding polymer composite material on the base of PA-6 with modifying additives that improve its injection properties: surface quality of moulded articles, filling of the mould and easier demoulding of finished articles; - 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.

2.2. Research methods

Polyamide-PLA biocomposites, hybrid modified by humic substances, were obtained by extruding pre-prepared raw materials in a single-screw laboratory extruder at a temperature of 170–200ºC and a roll rotation speed of 30–100 rpm.

Dynamic light scattering (Zetasaizer NanoZS, Malvern) was used to measure the size of nanoparticles in the humic substances, aqueous dispersions of colloidal polyelectrolyte humic substances with concentrations from $3\cdot10^{-4}$ g·mL^{-1} to $7\cdot10^{-5}$ g·mL^{-1} for humic substances were prepared.

The morphology of brown coal humic substances will be determined by transmission electron microscopy (TEM) using a Selmi EMV-125 TEM electron microscope. The research of impact strength and breaking stress during bending of the samples was carried out on a pendulum head according to GOST 4647 and GOST 9550, respectively.

3. Results and discussion

Start researching was performed to determine indicators of the quality of brown coal and humic substances. We used three different samples of brown coal to obtained humic substances. It should be noted that the brown coal samples are slightly different, namely:

- sample 3 was characterized by the highest content of analytical moisture at the level of 30,6%, the lowest content of analytical moisture was characteristic of sample 2 – 8,1%.
- in terms of ash content, the highest level was observed for sample 1 – 48,7%, the lowest for sample 2 – 8,3%;
- the total sulfur content ranged from 1,87 to 4,00% in a series of lignite samples 3>1>2;
- the maximum yield of volatile substances was characteristic of lignite samples 2 and 3 – 43,7%.

Indicators of elemental analysis and humic substances yield vary depending on the yield of volatile substances:

- the highest carbon content was characteristic of brown coal sample 1 – 80.83%;
- the oxygen content for brown coal of samples 2 and 3 was quite close - 24.11 and 29.12%, respectively.

Next researching was performed to determine indicators of the quality of coal humic substances (Table. 1).

It was performed the determination of the size of nanodispersed particles of humic substances by DLS. Since the particle size in the dispersed system depends on the concentration [36], the research was performed with solutions of different concentrations - Table. 2. Fig. 1 shows the data of microscopic studies of various samples of humic substances.

Based on the analysis data from Table 1 and Figure 1, it was found that for nanodispersed particles of obtained humic substances from brown coal by four different methods the size is from 52 nm to 38 nm.

Table 1. Indicators of the quality of coal humic substances*.

Sample	Output, %	Proximate analysis, % mas		Ultimate analysis, % mas		
		W^a	A^d	C^d	H^d	$N^d+S^d_t+O^d_d$
HS1	41.00	11.2	3.9	57.4	3.8	29.1
HS2	47.39	14.1	5.0	51.8	4.1	34.9
HS3	51.70	17.3	5.3	61.8	4.5	38.4

Table 2. Characteristics of nanoparticles of humic substances in polyelectrolyte dispersions.

Sample	C, g/mL^{-1}	Size ± SD, nm	PDI ± SD
HS1	3.5×10^{-4}	270 ± 22	0.93 ± 0.07
	3.6×10^{-5}	52 ± 2	1.00 ± 0.04
HS2	3.6×10^{-4}	368 ± 240	0.41 ± 0.02
	6.4×10^{-5}	310 ± 120	0.39 ± 0.08
HS3	3.5×10^{-4}	380 ± 25	0.94 ± 0.07
	3.6×10^{-5}	60± 9	1.00 ± 0.01

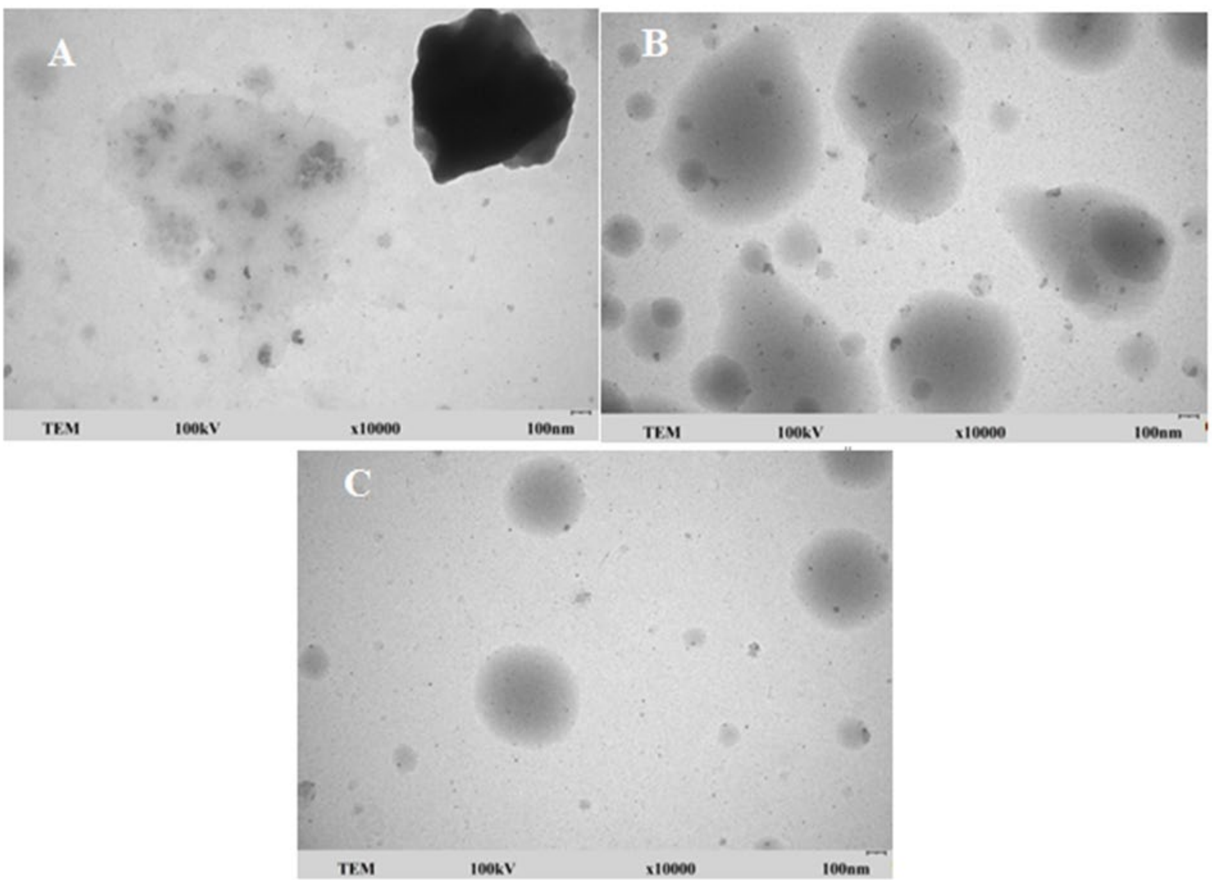

Fig. 1 Microscopic studies of humic substances from different types of lignite: A - HS1, B - HS2, B - HS3.

Further studies were aimed at the effect of the introduction of nanoparticles of humic substances on the complex of strength properties of the systems of polyamide-PLA biocomposite matrix - Fig. 1-2. From the results shown in Fig. 1-2, it is seen that the hybrid modification of polyamide-PLA biocomposite matrix with nanodispersed humic substances allows to obtain high-strength hybrid biopolymer composite materials, while the optimal content of nano dispersed humic substances in the polyamide-PLA biocomposite matrix is 0.5 % by mass. Due to the increase in the degree of crystallization and the emergence of intermolecular and ester bonds in the formation of a more rigid network structure in the polyamide-PLA-humic substances system there is an increase in mechanical properties of hybrid biopolymer nanocomposite materials in order humic substances №1< humic substances №2 <humic substances №3.

In fact, we can say that the production of biopolymer nanocomposites based on PLA and humic substances occurs by the mechanism of template synthesis to obtain a hybrid nanocomposite structure of materials.

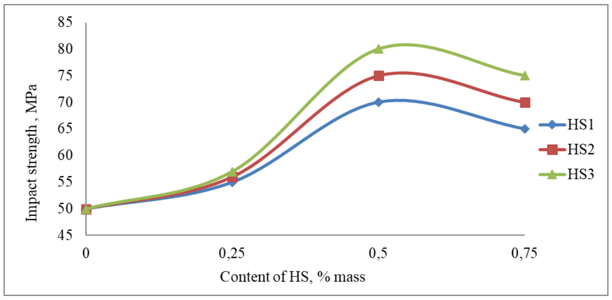

Fig. 2 Dependence of the impact strength of polyamide-polylactide– humic substances systems on the content of humic substances.

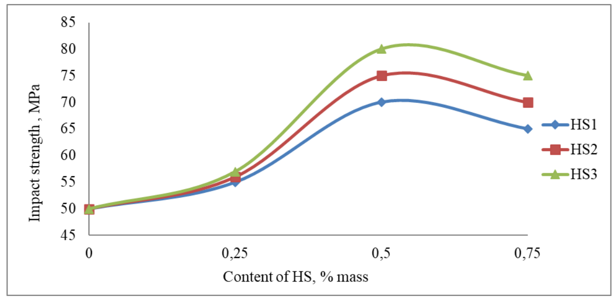

Fig. 3 Dependence of the breaking stress during bending of systems of PLA – humic substances on the content of humic substances.

4. Conclusions

Thus, article presents studies of new hybrid biocomposites based on polyamide, PLA and humic substances were developed and studied. The legal regulation peculiarities to ensuring environmental industrial enterprises' safety through the development of biocomposites technologies in Ukraine are considered. It has been established that humic substances, which were obtained from brown coals by extraction method, are characterized by nanodispersion in the range of 52-380 nm. It was found that due to the presence of a large number of active functional groups on the surface of such nanoparticles of humic substances is a hybrid modification of polyamide-PLA biocomposite by the mechanism of template synthesis, which is accompanied by an increase in the degree of crystallization and the formation of a more rigid polymer structure, which allows to obtain hybrid biopolymer nanocomposites with significant impact strength and breaking stress during bending. It was also found that the obtained hybrid biocomposites based on polyamide-PLA matrix and humic substances can be used to produce membrane-covering materials for wounds, implants, medical devices and products for dermatological treatment

Symbols

W^a	moisture contents, %;
A^d	ash content, %;
S^d_t	content of sulfur, %;
V^d	volatile matter, %;
C^d	content of carbon, %;
H^d	content of hydrogen, %;
N^d	content of nitrogen, %;
O^d_d	content of oxygen, %;
PDI	polydispersity.

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