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STUDY OF LIGNITE HUMIC ACIDS HYBRID MODIFICATION TECHNOLOGY OF BIODEGRADABLE FILMS BASED ON POLYVINYL ALCOHOL

Object of article study is lignite humic acids hybrid modification technology of biodegradable films based on polyvinyl alcohol. The possibility of increasing the strength and operational properties of biodegradable polymeric materials based on polyvinyl alcohol by using its modification with the different types of humic acids from lignite is considered. Lignite humic acids hybrid modification films with antibacterial properties were obtained. The two-stage technology of lignite humic acids hybrid modification of biodegradable films based on polyvinyl alcohol was formalized. At the first stage of lignite humic acids hybrid modification technologies for hybrid-modified biodegradable materials production, lignite humic acids are received. At the second stage, hybrid modification of lignite humic acids (that are part of biodegradable polyvinyl alcohol films), which are received by watering from a solution, takes place. It has been conducted a study on determining the effect of lignite humic acids hybrid modification on the most important operational properties of biodegradable film based on polyvinyl alcohol, i. e., tensile strength, relative elongation at break and time of mold appearance. Changes in tensile strength, relative elongation at break and time of mold appearance for the lignite humic acids hybrid modified biodegradable polymeric materials based on polyvinyl alcohol were revealed depending on the content of the different types of lignite humic acids. It was also shown that the lignite humic acids hybrid modification of polyvinyl alcohol with the different types of humic acids allows preserving the biodegradability of the films along with imparting the antibacterial properties. The developed lignite humic acids hybrid modified biodegradable polyvinyl alcohol films with antibacterial properties, in terms of their operational characteristics, are superior to the known similar biodegradable films based on natural biopolymers.

Keywords: *brown coal, humic acids, hybrid modification, polyvinyl alcohol, antibacterial properties, biodegradable films.*

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1. Introduction

In December 2017, the European Commission initiated a program on transitional coal regions as a stimulus action under the «Clean Energy for All Europeans» package [1]. Building on the work done under this package, in December 2019, the European Commission announced the European Green Agreement, an integral part of the Commission's strategy to support the EU's goal of achieving climate neutrality by 2050. The Transition Coal Initiative, extended to shale and peat mining regions in 2020, is a key building block of the European Green Agreement and Just Transition Mechanism. This level of ambition for the next decade will lead the EU on a balanced path to climate neutrality by 2050. This will require a fundamental restoration of our energy system balance, a shift to an accelerated abandonment of the «traditional» use of fossil fuels (coal, oil shale, peat), whose burning has the most negative environmental impact, and a more sustainable economic framework that potentially poses significant challenges for many regions [2]. The initiative for coal regions in transition in the Western Balkans and Ukraine was launched in December 2020 and aims to help countries and regions move away from coal to carbon-neutral economy, while ensuring the transition fairness. So, it is becoming necessary to determine the further use of fossil fuels in Ukraine, which would not cause a negative impact on the climate. To solve this task, it is advisable to analyze the available deposits of fossil fuels, as well as innovative technologies for their use [3].

Taking into account the natural antibacterial and antimicrobial properties as well as the relative ease of obtaining humic acids – lignite derivatives – they can be an ideal ingredient for the modification of biodegradable biopolymer films with enhanced antibacterial properties [4]. Studies [5, 6] have confirmed that the addition of antimicrobials, such as clove essential oil or oregano, has reduced the amount of yeast, mold and bacteria in starch films. It has also been found [6] that mixing starch with polyvinyl

alcohol (PVA) and alginate allows to obtain films that were more resistant to stretching and less hydrophilic than films containing only starch. Polyvinyl alcohol is a rather promising polymer for the production of biodegradable films – a universal polymer, the main chain of which contains C–C bonds, which contribute to its rapid biodegradation [7, 8]. In our previous works, the lignite humic acids hybrid modification (LHAHM) technology for biodegradable films based on polyvinyl alcohol [9] and hydroxypropyl methyl cellulose [10] have been developed and characterized. In these works, the possibility of developing and/or improving the antibacterial properties of the studied polymers has been demonstrated.

Hence, *this study aims* is to determining the effect of LHAHM technology on the strength and performance characteristics of PVA biodegradable films.

2. Materials and Methods

2.1. Materials. PVA (Kuraray, Japan) of the «Mowiol 6-98» (Clariant brand) was used as received.

The humic acids samples were used from lignite with different metamorphism degrees, from which humic acids have been produced.

2.2. Methods. The lignite humic acids hybrid modified biodegradable materials in the film form based on PVA were obtained by the watering method from PVA solutions (10 wt %) by dissolving the polymer in distilled water at a mass ratio of PVA:water as 10:100 at 363–373 K. To analyze the properties, PVA solutions were obtained at different concentrations of humic acids (5, 10, and 15 wt %).

The tensile strength properties of the lignite humic acids hybrid modified biodegradable materials in the film form based on PVA were determined according to ISO 527-2:2021. The tests were carried out on an IR 5040-5 tensile machine in the uniaxial tension mode at a temperature of 295 K. The speed of testing samples was 25 mm/min. The relative elongation at break (%) and tensile strength (MPa) were determined. Degree of biodegradation was evaluated according to DSTU EN 14995:2018 (EN 14995:2006, IDT) [11].

Antibacterial properties of biodegradable materials in the film form based on PVA were determined by the inhibition time of the active growth zones of *A. niger* molds on the their surface by using Digital Microscope HD color CMOS Sensor (China).

3. Results and Discussion

Based on studies [9, 10], the two-stage technology of lignite humic acids hybrid modification of biodegradable films based on PVA was formalized – Fig. 1. At the first stage of lignite humic acids hybrid modification technologies for hybrid-modified biodegradable materials production, lignite humic acids are received. At the second stage, hybrid modification of lignite humic acids (that are part of biodegradable polyvinyl alcohol films), which are received by watering from a solution, takes place. The first stage of the lignite humic acids hybrid modification technology includes the humic acids production from lignite by grinding it to obtain microparticles, preparing a suspension in a weak alkali solution and extraction, with mechanical suspension (humic acid coal microparticles) mixing in a reactor-mixer.

Actually, the first stage is a waste-free scheme of lignite processing into variety technological, ecological and economic products, which is in high demand, and includes:

– crushed and granulated sorbents (activated carbon) for industrial, home and wastewater purification from heavy metals, organic pollutants, water preparation for drinking water supply, process gases purification, hydrocarbon vapors recovery;

– lignite humic acids, as hybrid modifiers of biodegradable materials.

Liquid alkaline extract of lignite humic acids is received by extracting crushed lignite with an alkali aqueous solution and than centrifuged. The solid residue after centrifugation is used to granular sorbent production. Some part of lignite humic acids alkaline extract undergoes acid treatment and is sent to filtration with further drying in order to receive solid polydisperse lignite humic substances. The production stage of lignite humic acids and substances according to the presented technological scheme is waste-free, because the solid residue after coal extraction with alkali is sent to the granular sorbents production in the form of activated carbon. At the second stage of lignite humic acids hybrid modification of biodegradable films based on PVA, biodegradable films are received by watering from a PVA solution.

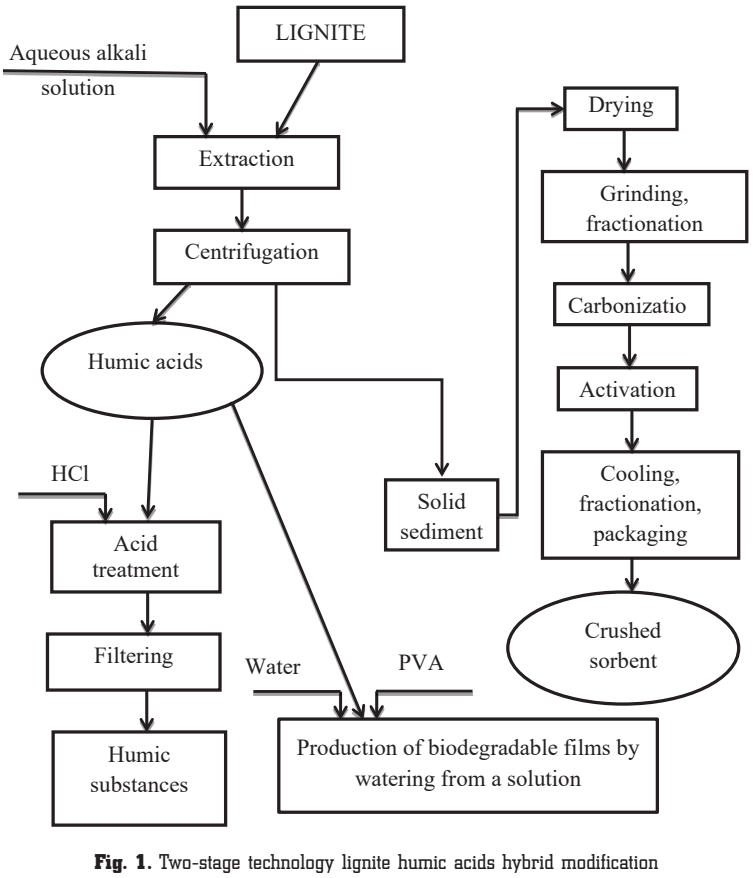

Fig. 1. Two-stage technology lignite humic acids hybrid modification biodegradable films based on PVA

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It has been conducted a study on determining the effect of LHAHM on the most important operational properties of biodegradable film based on PVA, i. e., tensile strength, relative elongation at break and time of mold appearance. Table 1 demonstrates how the above-mentioned parameters of the LHAHM films prepared from polyvinyl alcohol depend on the content of different type lignite humic acids.

Table 1

The effect of LHAHM on operational properties of biodegradable films based on PVA

Lignite sample	Humic acid content (% wt.)	Strength at break (MPa)	Relative elongation at break (%)	Mold appearance time (hours)
Pure PVA composition		20±0.2	18±0.2	24±2
HA1	5	22±0.2	19±0.2	72±2
	10	23±0.2	20±0.2	84±2
	15	23.5±0.2	21±0.2	96±2
HA2	5	21±0.2	22±0.2	56±2
	10	21.5±0.2	23±0.2	68±2
	15	22±0.2	24±0.2	80±2
HA3	5	25±0.2	24±0.2	168±2
	10	27±0.2	25±0.2	does not appear
	15	29±0.2	26±0.2	does not appear

Thus, it has been revealed that the LHAHM of biodegradable film based on PVA allows increasing the major strength characteristics along with imparting the antibacterial properties as evidenced by the findings on mold appearance time for the films. The effect of the LHAHM on the enhancement of the biodegradable film based on PVA characteristics for the different types of humic acids increases in the range HA1<HA2<HA3. This is due to the higher content of volatile acids in initial lignite 3 and the higher content of the polar C–O, O–H, C=O, and $–NH_2$ groups in the 3 sample of humic acids, as reported in our previous works [9, 10].

In order to determine the optimal content of humic acids, the biodegradability of lignite humic acids hybrid modified biodegradable film with antibacterial properties based on PVA has been examined as well (Fig. 2–4).

In general, it is clearly seen that the lignite humic acids hybrid modification of PVA for the development of biodegradable films with antibacterial properties allows preserving the biodegradability for the all types of used humic acids. According to the State Standard of Ukraine (DSTU EN 14995:2018), the weight loss of all samples exceeds 90 % within 6 months.

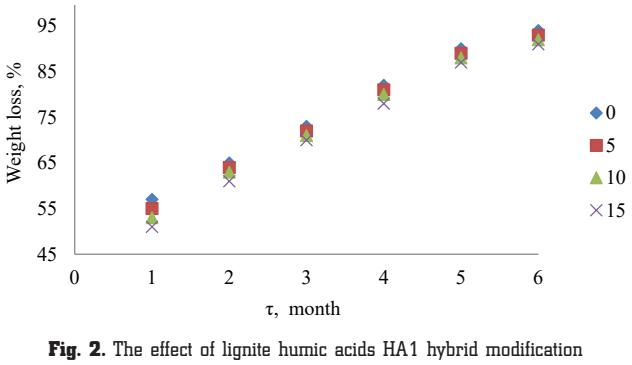

Fig. 2. The effect of lignite humic acids HA1 hybrid modification on degree of biodegradation of biodegradable film based on PVA with antibacterial properties

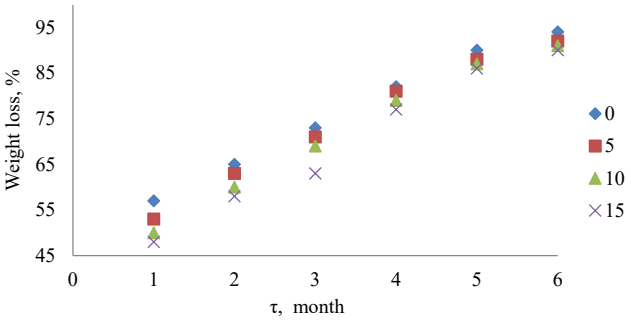

Fig. 3. The effect of lignite humic acids HA2 hybrid modification on degree of biodegradation of biodegradable film based on PVA with antibacterial properties

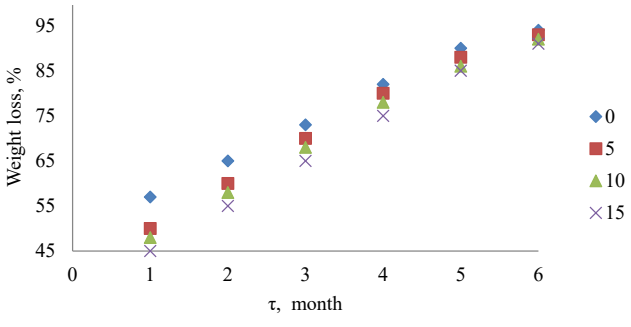

Fig. 4. The effect of lignite humic acids HA3 hybrid modification on degree of biodegradation of biodegradable film based on PVA with antibacterial properties

Practical significance of developed lignite humic acids hybrid modified biodegradable films with antibacterial properties based on PVA is using their as packaging materials for dry and food (bread, cereals, nuts, etc.) with an extended shelf life.

The limiting characteristics of the obtained lignite humic acids hybrid modified biodegradable films with antibacterial properties include the poor heat resistance of their packaging when using wet products – no more than 90–100 °C. Also the next limitation factor in the conditions of martial law is associated with an increase in logistical difficulties of delivery and the price of the foreign raw materials in the form of PVA during lignite humic acids hybrid modified biodegradable films with antibacterial properties production.

The main prospects for further research include the determination of the effectiveness of antibacterial action developed in relation to different types of products for packaging.

4. Conclusions

The two-stage technology of lignite humic acids hybrid modification of biodegradable films based on PVA was formalized. At the first stage of lignite humic acids hybrid modification technologies for hybrid-modified biodegradable materials production, lignite humic acids are received. At the second stage, hybrid modification of lignite humic acids of biodegradable PVA films takes place.

It has been found that the hybrid modification by lignite humic acids of PVA by the mechanism of a matrix synthesis for the development of biodegradable films allows increasing the major strength characteristics along with imparting the antibacterial properties as evidenced by the findings on mold appearance time for the films.

It has been also shown that the lignite humic acids hybrid modification of PVA of different types for imparting antibacterial properties at the level of 250 hours of the onset of mold ensures the film biodegradability exceeding 91 % within 6 months at the optimal content of humic acids of 10 wt %.

Due to their operational characteristics, the developed lignite humic acids hybrid modified biodegradable films with antibacterial properties based on PVA are promising candidates for packaging materials for dry and food (bread, cereals, nuts, etc.) with an extended shelf life.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

Manuscript has no associated data.

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