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REGULARITIES OF CLEANING AND DEWATERING OF GAS CLEANING SLUDGE FROM COAL DUST AT THERMAL POWER PLANTS (p. 6–15)

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The object of this study is the technology of cleaning and dewatering of sludges from wet gas purification systems of dust preparation department emissions in Ecomash SHS521AS-113 settling centrifuges in order to solve the problem of increasing the efficiency of treatment facilities and secondary use of purified water.

Samples of gas purification sludges have been analyzed under industrial conditions, and it was found that sludges from thermal power plants contain finely dispersed dust particles less than 20 microns, which during the hydration process stick together into aggregates up to 250 microns in size.

It was found that the use of settling tanks without chemical reinforcement of the process is long-term; however, they are effectively precipitated using the anionic flocculant A-19. The optimal dose of flocculant for sludges with a concentration of 20–30 g/l was selected, which was 130–150 g/t. In this case, flocs are formed with a sedimentation rate of 8.2–8.6 mm/s, which is sufficient for effective settling. In order to quickly determine the concentration of the solid phase in the sludge, a relationship was established between the concentration of the dispersed phase, the temperature in the range of 20–45°C, and the density of the sludge.

The study of sludge purification in centrifuges without the use of reagents has made it possible to identify the relationship between the efficiency of solid phase retention, centrifuge productivity, and the value of the relative screw revolutions. It was found that the efficiency of solid phase retention in centrifuges increases with a decrease in work productivity, as well as a decrease in the value of the relative screw revolutions. The purification productivity of up to 15–20 m³/h was achieved with an efficiency of over 97% and a residual concentration of suspended particles of less than 0.5 g/l. The use of a modular sludge purification and dewatering unit based on a thin-layer clarifier and centrifugal units with the introduction of a flocculant before the clarifier has been proposed. It was found that the degree of sludge

dehydration in Ecomash SHS521AS-113 centrifuges of wet gas treatment sludge was 32–36%.

Keywords: coal dust emissions, coal sludge, dehydration efficiency, gas treatment sludge purification, environmental safety.

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ESTABLISHING REGULARITIES OF FIRE PROTECTION OF WOOD BY A COMPOSITE COATING WITH A BIOPOLYMER (p. 16–25)

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The object of this study is changes in the surface properties of wood during its treatment with a fire-retardant composite coating with the presence of biopolymers. The task, aimed at the production of environmentally friendly compositions obtained from natural and renewable sources for fire protection of wood and the application technology, is to ensure resistance to the action of high-temperature flames.

It has been proven that the fire-retardant composition with the presence of biopolymers is an accumulation of biological substances with nitrogen-phosphorus flame retardants, carbohydrates, and gas-forming substances, bordered by a polymer binder. Under the influence of thermal action, chemical reactions begin in the fire-retardant composition, ammonium polyphosphate decomposes and releases phosphoric acid. This, in turn, affects the destruction of the biopolymer and the dehydration of pentaerythritol with the formation of a large amount of hydrocarbons, and melamine causes the release of non-combustible gases, which induce the formation of foam coke.

A study of the surface energy characteristics of the fire-retardant composition with the presence of biopolymers was carried out and it was found that the polarity of the fire-retardant composition with the presence of biopolymers exceeds the value of untreated wood by 3.5 times, which provides effective treatment of the wood surface. According to the results of thermal exposure to the samples, it was found that under the action of the radiation panel, the fire-retardant composition swelled, when biopolymers such as wood flour and starch were added, the coke height increased by more than 15 mm, and the foam multiplicity increased by 1.2 times.

The practical significance is that the results were taken into account when designing a reactive coating for wood. Thus, there is reason to argue about the possibility of effective protection of wood with a fire retardant composition with the presence of biopolymers.

Keywords: fire retardant composition, biopolymers, wood surface treatment, surface tension, coating swelling.

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DETERMINING THE FIREPROOF LIMIT FOR THE HEAT PROTECTIVE COATING OF THE GAS GENERATOR IN A HYDROGEN STORAGE AND SUPPLY SYSTEM (p. 26–34)

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This work considers the task to prevent fires in hydrogen storage and operation systems. The subject of the study is the properties of the heat-protective coating of the gas generator in the hydrogen storage and supply system. The fire resistance limit is used as such a property. The set of heat-protective coating and the wall of the gas generator is considered as a thermodynamic system with two inputs. The signal at one input reflects the influence of thermal factors of the fire, and the signal at the second input corresponds to the thermal state of the gas generator cavity.

A mathematical description of such a thermodynamic system has been constructed, which is represented in operator form using the integral Laplace transform. A feature of such a mathematical notation is that it includes hyperbolic functions of an irrational argument. An approximation of mathematical models of the thermodynamic system was carried out and it is shown that these models, which are transfer functions, belong to fractional-rational functions with third-order Hurwitz polynomials. The approximation accuracy is 3.8%.

An expression for the reaction of a thermodynamic system has been derived, provided that the influence of thermal factors of a fire is described by an arbitrary function of time, and the thermal state of the gas generator cavity is described by the Heaviside function. To construct this expression, the Borel theorem and auxiliary functions are used, the parameters of which are the parameters of the roots of the algebraic Hurwitz equation.

Examples of determining the fire resistance limit for the heat-protective coating of the gas generator in the hydrogen storage and supply system for the characteristic conditions of its operation are given. It is shown that the fire resistance limit of such a coating is 462.8 s at a critical temperature of 320°C under the condition that the influence of thermal factors of a fire is linear (the generalized temperature change rate is 2.0°C s⁻¹). In this case, the thermal state of the gas generator cavity is stationary and is characterized by a temperature of 60°C.

Keywords: hydrogen systems, gas generator, fire, heat-protective coating, fire resistance limit, Laplace transform.

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ЗАКОНОМІРНОСТІ ОЧИЩЕННЯ ТА ЗНЕВОДНЕННЯ ШЛАМІВ ГАЗООЧИЩЕННЯ ТЕПЛОВИХ ЕЛЕКТРОСТАНЦІЙ ВІД ВУГІЛЬНОГО ПИЛУ (с. 6–15)

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Об'єктом дослідження є технологія очищення та зневоднення шламів систем мокрого газоочищення викидів пилопідготовчого відділення в осаджувальних центрифугах Ecomash SHS521AS-113 задля вирішення проблеми підвищення ефективності роботи очисних споруд та вторинного використання очищеної води. Проаналізовано в промислових умовах зразки шламів газоочищення та встановлено, що шлами теплових електростанцій містять дрібнодисперсні частинки пилу менше 20 мкм, які в процесі гідратації злипаються у агрегати розміром до 250 мкм. Встановлено, що використання відстійників без хімічного підсилення процесу є довготривалим, однак ефективно осаджуються з використанням аніонного флокулянту А-19. Підібрано оптимальну дозу флокулянту для шламів концентрацією 20–30 г/л, яка склала 130–150 г/т. При цьому утворюються флокули зі швидкістю осідання 8,2–8,6 мм/с, що достатньо для ефективного відстоювання. З метою оперативного визначення концентрації твердої фази в шламів встановлена залежність між концентрацією дисперсної фази, температурою в інтервалі 20–45°C та густиною шламу. Проведене дослідження очищення шламів в центрифугах без використання реагентів дозволило виявити залежність між ефективністю затримання твердої фази, продуктивністю центрифуг та величини відносних обертів шнеку. Виявлено, що ефективність затримання твердої фази у центрифугах підвищується із зниженням продуктивності роботи, а також зниженням величини відносних обертів шнеку. Було досягнуто продуктивність очистки до 15–20 м³/год при ефективності понад 97% і залишкової концентрації завислих частинок менш ніж 0,5 г/л. Запропоновано використання модульної установки очистки та зневоднення шламів на базі тонкошарового відстійника та центрифугальних установок із введенням флокулянту перед відстійником. Встановлено, що ступінь зневоднення осаду у центрифугах Ecomash SHS521AS-113 шламів мокрої газоочистки складала 32–36%.

Ключові слова: викиди вугільного пилу, вугільні шлами, ефективність зневоднення, очищення шламів газоочищення, екологічна безпека.

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ВСТАНОВЛЕННЯ ЗАКОНОМІРНОСТЕЙ ВОГНЕЗАХИСТУ ДЕРЕВИНИ КОМПОЗИТНИМ ПОКРИТТЯМ З БІОПОЛІМЕРОМ (с. 16–25)

Ю. В. Цапко, О. Ю. Цапко, Р. В. Ліхнівський, К. Г. Белікова, О. Ю. Бердник, А. Ф. Гаврилюк, А. С. Борисова, О. Г. Доценко, М. О. Гайдук, В. В. Нестеренко

Об'єктом досліджень є зміни поверхневих властивостей деревини під час її оброблення вогнезахисним композиційним покриттям з наявністю біополімерів. Проблема, спрямована на виробництво екологічно-чистих композицій, отриманих з природних та відновлюваних джерел для вогнезахисту деревини та технологією нанесення, полягає у забезпеченні стійкості до дії високотемпературного полум'я. Доведено, що вогнезахисна композиція з наявністю біополімерів є нагромадженням біологічних речовин з азотно-фосфорними антипіренами, вуглеводами та газотворючими речовинами, облямованих полімерним в'язучим. Під впливом термічної дії розпочинаються хімічні реакції у вогнезахисній композиції, поліфосфат амонію розкладається і виділяє фосфорну кислоту. Це, у свою чергу, впливає на деструкцію біополімеру та дегідратацію пентаерітриру з утворенням великої кількості вуглеводнів, а меламін проваджує виділення негорючих газів, що спонукають утворювати пінокок. Проведено дослідження поверхневих енергетичних характеристик вогнезахисної композиції з наявністю біополімерів та встановлено, що полярність вогнезахисної композиції з наявністю біополімерів перевищує значення необробленої деревини у 3,5 рази, що дає ефективне оброблення поверхні деревини. За результатами термічного впливу на зразки встановлено, що при дії радіаційної панелі відбулося спучення вогнезахисної композиції, при додаванні біополімерів, таких як деревне борошно і крохмаль, висота коксу підвищилась понад 15 мм, а кратність піни підвищилась в 1,2 рази. Практичне значення полягає у тому, що отримані результати було враховано під час розроблення реактивного покриття для деревини. Таким чином, є підстави стверджувати про можливість ефективного захисту деревини вогнезахисною композицією з наявністю біополімерів.

Ключові слова: вогнезахисна композиція, біополімери, оброблення поверхні деревини, поверхневий натяг, спучення покриття.

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ВИЗНАЧЕННЯ МЕЖІ ВОГНЕСТІЙКОСТІ ТЕПЛОЗАХИСНОГО ПОКРИТТЯ ГАЗОГЕНЕРАТОРА СИСТЕМИ ЗБЕРІГАННЯ ТА ПОДАЧІ ВОДНЮ (с. 26–34)

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Роботу присвячено проблемі запобігання пожеж в системах зберігання і експлуатації водню. Предметом дослідження є властивості теплозахисного покриття газогенератора системи зберігання та подачі водню. В якості такої властивості викорис-

товується межа вогнестійкості. Сукупність теплозахисного покриття і стінки газогенератора розглядається як термодинамічна система, яка має два входи. Сигнал на одному вході відображає вплив теплових чинників пожежі, а сигнал на другому вході відповідає тепловому стану порожнини газогенератора. Побудовано математичний опис такої термодинамічної системи, який представлено в операторній формі із використанням інтегрального перетворення Лапласа. Особливістю такого математичного опису є те, що він включає гіперболічні функції ірраціонального аргументу. Здійснено апроксимацію математичних моделей термодинамічної системи і показано, що ці моделі, які є передаточними функціями, належать до дробово-раціональних функцій із поліномами Гурвіца третього порядку. Точність апроксимації складає 3,8%. Одержано вираз для реакції термодинамічної системи за умови, що вплив теплових чинників пожежі описується довільною функцією часу, а тепловий стан порожнини газогенератора описується функцією Хевісайда. Для побудови цього виразу використовується теорема Бореля та допоміжні функції, параметрами яких є параметри коренів алгебраїчного рівняння Гурвіца. Наведено приклади визначення межі вогнестійкості теплозахисного покриття газогенератора системи зберігання та подачі водню для характерних умов її експлуатації. Показано, що межа вогнестійкості такого покриття складає 462,8 с при критичній температурі 320°C за умов, що вплив теплових чинників пожежі має лінійний характер (узагальнена швидкість зміни температури складає $2,0^{\circ}\text{C}\cdot\text{s}^{-1}$). При цьому тепловий стан порожнини газогенератора є стаціонарним і характеризується температурою 60°C.

Ключові слова: водневі системи, газогенератор, пожежа, теплозахисне покриття, межа вогнестійкості, перетворення Лапласа.

The object of this study is changes in the surface properties of wood during its treatment with a fire-retardant composite coating with the presence of biopolymers. The task, aimed at the production of environmentally friendly compositions obtained from natural and renewable sources for fire protection of wood and the application technology, is to ensure resistance to the action of high-temperature flames.

It has been proven that the fire-retardant composition with the presence of biopolymers is an accumulation of biological substances with nitrogen-phosphorus flame retardants, carbohydrates, and gas-forming substances, bordered by a polymer binder. Under the influence of thermal action, chemical reactions begin in the fire-retardant composition, ammonium polyphosphate decomposes and releases phosphoric acid. This, in turn, affects the destruction of the biopolymer and the dehydration of pentaerythritol with the formation of a large amount of hydrocarbons, and melamine causes the release of non-combustible gases, which induce the formation of foam coke.

A study of the surface energy characteristics of the fire-retardant composition with the presence of biopolymers was carried out and it was found that the polarity of the fire-retardant composition with the presence of biopolymers exceeds the value of untreated wood by 3.5 times, which provides effective treatment of the wood surface. According to the results of thermal exposure to the samples, it was found that under the action of the radiation panel, the fire-retardant composition swelled, when biopolymers such as wood flour and starch were added, the coke height increased by more than 15 mm, and the foam multiplicity increased by 1.2 times.

The practical significance is that the results were taken into account when designing a reactive coating for wood. Thus, there is reason to argue about the possibility of effective protection of wood with a fire retardant composition with the presence of biopolymers

Keywords: fire retardant composition, biopolymers, wood surface treatment, surface tension, coating swelling

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ESTABLISHING REGULARITIES OF FIRE PROTECTION OF WOOD BY A COMPOSITE COATING WITH A BIOPOLYMER

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1. Introduction

Wood is one of the most common building materials and is one of the most affordable and renewable materials, which

is easily processed, has acceptable mechanical properties, appearance, as well as environmental and sanitary aspects. However, the use of timber in the construction industry is regulated by fire and environmental safety rules because

it is a fire-hazardous material. Thus, when burning, wood spreads flame over the surface, is capable of producing smoke and releasing toxic combustion products, which can harm human health. Thus, wood needs protection from fire.

The most common fire protection agents used for wooden structures include inexpensive organic and inorganic compounds in their formulations. However, individual chemicals, as well as their combustion products, are highly toxic substances, and their use is prohibited. It should be noted that fire retardants can be used as impregnation or coating, have a short service life and low resistance to external temperature and humidity influences. In addition, during the operation of building structures, these agents change the structure and appearance of wood, so it is necessary to repeat the application of these products to ensure long-term protection. In this regard, the need for work in this direction is determined, with special attention to the development of effective fire retardant coatings for their use during the construction of general construction objects, where the use of fire retardant mixtures is ineffective.

Accordingly, research in the area of fire protection of wood is aimed at the production of non-toxic and environmentally friendly compositions. They are obtained from natural and renewable sources, which can gradually replace classic flame retardants and formulations based on them, while maintaining the fire protection characteristics and properties of wood.

However, there is a movement towards effective biorefinery processes, which offers the possibility of using biological substances as an environmentally safe green variety for fire-retardant materials. A significant number of biological compounds such as polysaccharides, aromatic compounds, proteins, and others have shown their ability to form carbon. They can form a thermal insulation barrier that will protect wood by reducing oxygen diffusion and heat transfer, as well as the intensive formation of volatile combustible products that participate in the combustion of wood. The combination of these biological substances with flame retardants containing phosphorus and nitrogen provides an effective way to enhance the action of modern fire protection systems containing polyphosphoric flame retardants, carbohydrates, and foaming agents.

Therefore, research into the production of compositions with biopolymers and determining the influence of the components that make up their composition on fire protection is relevant.

2. Literature review and problem statement

Study [1] proposes a sustainable approach to enhance the fire resistance and smoke suppression of poly(lactic acid) (PLA)-based composites. This contributes to solving one of the main problems of biocomposites that limits their application in various engineering sectors such as automotive and construction industries. Flax fibers (FFs) were surface-functionalized with a novel organic-inorganic hybrid flame retardant (FR), which offers a sustainable bio-inspired approach. It specifically mitigates the potential degradation of mechanical properties and leaching of FR, which can cause environmental problems and reduce the durability of the composite. First, flax fibers (FFs) are pre-treated with ozone to promote the formation of carboxyl groups (FF-O3); then gallic acid (GA) units are covalently immobilized on the

fiber surface (FF-GA); finally, the hybrid iron phenyl phosphonate FR forms a complex with the phenolic groups of the GA units (FF-GA-FeP). Fourier transform infrared (FT-IR) analysis of FF-GA-FeP confirmed the presence of specific absorption associated with the applied FR coating. Scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS) revealed changes in the morphology of the fibers and confirmed the incorporation of iron and phosphorus. Solid-state nuclear magnetic resonance spectroscopy (SSNMR) and X-ray WAXS microscopy showed that the crystallinity of the fibers was not significantly affected by derivatization. Microwave plasma atomic emission spectroscopy (MP-AES) revealed a precise iron loading of 0.1 wt%. The use of FF-GA-FeP as a reinforcing material in PLA-based composites (PLA/FF-FeP) resulted in enhanced thermal stability and fire resistance of the composites with minimal coating, as revealed by thermogravimetric analysis (TGA) and cone calorimetric tests (CCT). For PLA/FF-FeP, a reduction of 5, 87, 68, and 9.5% in peak heat release rate (pHRR), total smoke release (TSR), specific extinction area (SEA), and flame spread index (FPI) was achieved, respectively, compared to untreated PLA reinforced with flax fiber (PLA/FF). In addition, preliminary tensile tests indicate a slight change in tensile strength and a slight increase in stiffness of PLA/FF-FeP compared to PLA/FF. Therefore, in a biocomposite, immobilization of a minimal amount of iron phenyl phosphonate directly on the surface of flax fiber has been shown to be an effective strategy for smoke suppression while maintaining the mechanical integrity of the composite. However, the optimal conditions for its use have not been established.

In [2], epoxy resin, triethyl phosphate (TEP), and polyethylene glycol (PEG) were investigated, which were introduced into a delignified balsa wood template by vacuum pressure impregnation. And a TW/PEG/TEP biocomposite was obtained, which combines fire resistance, high strength, and energy storage characteristics during phase transition. TW/PEG composites have no leakage during the phase transition process, and their transparency is up to 95%. Compared with TW/PEG, the shielding effect of the carbon layer and the braking effect in the condensed and gas phases significantly reduce the total heat release of TW/PEG/TEP. TW/PEG/TEP biocomposites still maintained a high phase transition enthalpy and a low peak melting temperature, which contributed to their application in the field of low-temperature energy storage during phase transition. In addition, the tensile strength of TW/PEG/TEP was nearly 4 times higher than that of DW, and their viscosity was significantly increased. TW/PEG/TEP biocomposites meet the modern concept of energy conservation and green development. They have the potential to replace traditional materials and show excellent application prospects in new industries. However, it is not revealed how they affect the environment.

In [3], the thermal and kinetic characteristics of bio-epoxy composites in an oxidizing atmosphere are investigated. The main objective is to evaluate the thermomechanical behavior of such materials for heat transfer purposes in aggressive/corrosive environments. For this purpose, two parameters were chosen to describe the effect of (1) the flame retardant coating as a flame retardant and (2) the SiC powder as a filler to improve thermal conductivity. Several samples were first fabricated using the vacuum bag resin transfer (VBRTM) process and then analyzed using thermogravimetric analysis in an oxidizing atmosphere. The comparison results show that the proposed flame retardant material has a positive

effect in terms of flame retardant. In addition, the loading of SiC powder has a great potential to improve thermal conductivity without affecting the mass loss rate. However, their impact on the ecosystem is not specified.

In [4], the flame retardant materials and the flame retardant process are considered in a two-pronged approach. An environmentally friendly biological synergistic flame retardant (PAU) was synthesized based on phytic acid (PAU) and urea (U) by simple complexation in water. The developed flame retardant coating can be directly applied to the surface of any topological shape with polydopamine as an adhesive. With the developed PAU flame retardant coating, a flame retardant expanded polystyrene (EPS-PAU) with light weight and high strength is produced. The coated EPS boards have a V-0 UL-94 rating and a limited oxygen index of 42.0% and excellent smoke suppression. Moreover, the density of EPS-PAU is only slightly increased by 2.27% compared with pure EPS, and the hard shell formed using PDA as an adhesive layer contributes to the improvement of impact strength. This new biomass-based PAU system offers a promising strategy for the production of polymer products with excellent flame retardancy, smoke inhibition, and light weight. But it is not known how it affects the mitigation of the flame.

In [5], a promising biodegradable polymer, cellulose triacetate (CTA), was synthesized and plasticized with ionic liquids to obtain flexible biocomposite films for multipurpose use. Initially, the CTA polymer was synthesized from industrial cotton waste by a heterogeneous route. Subsequently, four ionic liquids were synthesized, namely: 3-hexyl-1-methylimidazolium acetate [C6MIM][Ac], 3-hexyl-1-methylimidazolium hexafluorophosphate [C6MIM][PF6], N-hexyl N,N,N-triethylammonium acetate [N2226][Ac] and N-hexyl N,N,N-triethylammonium hexafluorophosphate [N2226][PF6], which were used as plasticizers for the CTA film. Morphological results showed that the obtained films had smooth surfaces and high transparency. The addition of ionic liquids significantly reduced the crystallinity of the CTA film and made it plastic. The results of mechanical and thermal tests showed that the anion of the ionic liquid has a significant effect on the film properties. The CTA films plasticized with [PF6]—based ionic liquids were more flexible than the others, with an elongation of 18.22% instead of 1.97%. The climatic aging test, on the other hand, confirmed that the used ionic liquids could indeed maintain the plasticized state during aging with a better stability of the hydrophobic ionic liquid in the polymer matrix compared to the hydrophilic ionic liquid. They self-extinguish with a final residue of about 97 wt.%, which allows the use of CTA films for thermal insulation and fire protection, as well as for packaging. However, it is not known how the coating is operated.

In [6], it is stated that biocomposites reinforced with natural fibers are an environmentally friendly and inexpensive alternative to traditional petroleum-based materials. Combustion of biocomposites can create life-threatening conditions in buildings, leading to significant human and material losses. Additives known as flame retardants (FRs) are widely used to improve the fire resistance of wood and biocomposites, textiles and other industries in order to expand their applications. Currently, this practice is very common in the construction sector due to strict fire safety regulations for residential and public buildings. To create a holistic picture, the flammability of wood and natural fibers as material resources for the production of biocomposites was investigated. In addition, the potential of lignin as an environmentally

friendly and inexpensive fire-resistant additive for the production of high-performance biocomposites with improved technological and fire-resistant properties was discussed in detail. The development of sustainable fire-resistant systems based on renewable raw materials represents a viable and promising approach to produce biocomposites with improved fire resistance, lower environmental impact, and improved health and safety performance. However, it is not stated how their properties change during service life.

In [7], efforts are made to characterize and use such renewable materials as alternatives to wood-based construction products. In addition, industrial wastes such as fly ash (FA) and peanut shell ash (PSA) are used to produce value-added composite materials. The addition of banana fiber, jute fiber, and natural resin resulted in a reduction in water absorption from 24% to 1.2% and a 12-fold improvement in mechanical properties compared to particleboard and teak wood. The addition of peanut ash showed an improved abrasion resistance of 1.25 times. The proposed composite material, reinforced with natural fiber and industrial waste, has certain mechanical properties, better resistance to water absorption, wear, fire resistance and weathering than particleboard and teak wood. However, a key role in their resistance under severe fire exposure has not been noted.

In [8], the effect of natural (NV) and expanded (EV) vermiculite clays on the properties of bio polyethylene (BioPE)-vermiculite clay biocomposites was investigated. It was observed that the addition of NV and EV clays to BioPE increased the thermal deflection temperature (HDT) and improved the fire resistance. In general, the degree of crystallinity (X_c) of BioPE decreased with increasing NV clay content, however, in the presence of EV clay, a decrease in X_c was observed only for EV clay contents above 3 phr. By optical microscopy, it was observed that EV clay particles were better dispersed in the BioPE matrix, while many NV clay agglomerates were formed. SEM micrographs showed a lack of adhesion between the BioPE matrix and NV or EV clay, which resulted in a decrease in tensile strength and impact strength. Rheological measurements under oscillatory shear flow conditions showed the formation of a percolated network structure in the BioPE-NV and BioPE-EV biocomposites containing 5 and 10 wt. parts of NV or EV clay. The biocomposite containing 10 wt. parts of EV clay showed a higher melt yield strength. Rheological measurements at high shear rates showed that the processability of the biocomposites would be similar to that of pure BioPE. However, it is not stated what accounts for the good thermal insulation and thermal stability.

As stated in [9], biocomposites are usually formed by binding natural fibers obtained from plants or cellulose with organic binders. The fibers used are usually industrial by-products, so they are common and inexpensive. One such material is sawdust and varieties of composite boards are made using sawdust as a filler. Both the matrix and the sawdust are flammable, and this article also discusses the use of an inorganic matrix to improve fire resistance. The inorganic matrix can withstand temperatures up to 1000°C and provides protection against sawdust for a short period of time. The strength of these plates was increased by reinforcing them with a very low percentage of high-strength glass and carbon fibers. Since these fibers provide a fifteen-fold increase in strength, the increase in cost is justified. Prisms were fabricated using various proportions of sawdust from approximately 11% to 38% by weight. The prisms were tested

in compression and flexure to obtain basic mechanical properties and determine the optimum sawdust content. Prisms with the optimum sawdust content were also reinforced with glass or carbon fibers to increase flexural strength. The results show that it is possible to fabricate and design these types of composite beams to achieve the desired strength without the use of special equipment, heat, or pressure. Thus, creating an environmentally friendly biocomposite material. However, nothing is said about the environmental friendliness of these products.

In [10], it was noted that different types of starch were used in the matrix of biocomposites: potato, sweet potato, and corn. Natural fibers, including jute, sisal, and kaboua, were used as discrete reinforcement. Water and glycols were used as plasticizers. Injection-molded samples were fabricated and characterized by various methods. Differential scanning calorimetry (DSC) and thermogravimetry (TGA) were used to characterize the thermal behavior of these composites. The treated samples did not show the typical endothermic peak observed in DSC scanning for starch powder. No significant difference in weight loss and decomposition due to fiber or plasticizer content was observed between different samples. Attenuated total reflectance infrared (ATR-IR) spectroscopy was used to characterize starch compounds and the influence of plasticizers and reinforcing fibers. The spectra obtained for most samples were consistent with the spectra of pure starch. Scanning electron microscopy (SEM) images showed the morphology of samples for different types of starch matrices and different fiber contents. However, the values of these parameters do not cover a significant range of their application.

Thus, from the literature [2, 4, 5, 7, 9, 10] it was established that fire retardant compositions with the presence of biopolymers are able to protect wood from fire during operation, but the parameters that ensure their resistance to thermal effects have not been determined. Therefore, the establishment of parameters for wood protection and the influence of mixtures of flame retardants with biopolymers on this process necessitated the need for research in this area.

3. The aim and objectives of the study

The aim of our work is to identify the patterns of fire protection of wood during thermal exposure to wood, fire-protected by a composite coating with a biopolymer. This makes it possible to reduce the load of chemicals in the fire-retardant composition for wood.

To achieve the goal, the following tasks were set:

- to investigate the process of forming a composite coating when adding biopolymers;
- to establish the features of the formation of surface characteristics when adding biopolymers to the composite coating and changes in the formation of the thermal insulation layer of foam coke wood during processing.

4. The study materials and methods

4.1. The object and hypothesis of the study

The object of our study is the process of changing the surface properties of wood when it is treated with a fire-retardant composite coating with the presence of biopolymers. The scientific hypothesis assumes the change in surface and

interfacial tension when applying a fire-retardant composite coating with the presence of biopolymers to wood. In the process of the study, it was assumed that the course of the process of treating wood with a fire-retardant composite with a biopolymer is constant under the influence of external conditions. It was simplified that the temperature, humidity, and pressure of the wood treatment process do not change.

4.2. The materials under study used in the experiment

To establish the feasibility of using a fire-retardant composition with the presence of biopolymers, pine wood samples were used, on which a coating was applied. This base coating consists of a mixture of ammonium polyphosphate, pentaerythritol, melamine, chloroparaffin, titanium dioxide, which were dissolved in acrylic resin. Biopolymers were added to the coating, in particular, wood flour in an amount of 10% (wt.), starch in an amount of 9% (wt.), coffee grounds in an amount of 7% (wt.). The resulting coating was tested after intensive mixing.

At the first stage, to study the structure of the composition with a biopolymer, samples were prepared based on wood flour with a coating in a ratio of 1:1. The nature of the interaction of the fire-retardant composition with the presence of biopolymers with wood was also studied. To establish the surface characteristics of the composition with biopolymer and to establish the contact angle, pine wood samples measuring 50×50×10 mm were made. To determine the swelling ability, wood samples measuring 40×40×10 mm were used, which were coated with the above coating with a consumption of approximately 250÷260 g/m². The film thickness was within 0.5÷0.6 mm. After the samples were aged for two weeks, swelling ability tests were performed.

4.3. Methods for studying the properties of a flame retardant composition with the presence of biopolymers

The structure of a flame retardant composition with the presence of biopolymers was determined by Fourier transform infrared spectroscopy (FTIR) and identification by thermogravimetric analysis.

Fourier transform infrared spectroscopy (FTIR) was performed taking into account [11]. The analysis was performed on a Spectrum One spectrometer (Perkin Elmer) (USA).

Thermogravimetric analysis was performed on a Linseis STA 1400 derivatograph (Germany) according to [12]. Samples weighing 10 mg were heated in an air atmosphere from 20 to 700°C at a rate of 10°C/min.

The surface tension of a flame retardant composition with the presence of biopolymers was determined by the ring detachment method (Du-Nooyi) [13]. The liquid under study was placed in a cuvette and installed on a torsion balance. A metal ring was placed in the liquid and after its immersion it was gradually pulled out, controlling the value of the scale on the scales.

Tests to determine the contact angle were carried out according to the methodology from [14]. Its essence was to apply a drop of coating to the substrate of the test material and after the drop reached an equilibrium state, the contact angle was determined using a microscope.

To estimate the surface energy of aqueous solutions of mixtures of inorganic salts and fire-retardant wood during coating, the Fowkes method was used, which makes it possible to take into account dispersion, hydrogen, and dipole-dipole interactions at the solid-liquid interface [14]

$$(1 + \cos \theta) \sigma_{sa} = 2 \left(\sigma_{sa}^d \cdot \sigma_{la}^d \right)^{0.5} + 2 \left(\sigma_{sa}^p \cdot \sigma_{la}^p \right)^{0.5}, \quad (1)$$

where θ is the edge wetting angle;

σ_{sa} , σ_{la} – surface energy of solid and liquid, respectively; the p index is the component of the total surface energy due to hydrogen and dipole-dipole interactions; index d – due to dispersion interactions.

This equation has two unknown quantities σ_{sa}^d and σ_{sa}^p and for practical use, contact angle data for two different test materials with known surface tensions σ_{la}^d and σ_{la}^p are required (Tables 1).

Table 1

Surface tension and dispersed and polar components for test materials

Material	Surface energy of a solid		Surface tension, σ_{sa} , mJ/m ²
	Dispersion, σ_{sa}^d , mJ/m ²	Polar, σ_{sa}^p , mJ/m ²	
Glass	8.1	33.9	42.0
Polyvinyl chloride	41.2	1.4	42.6

The study of the process of formation of a swollen layer of foam coke of a fire-retardant composition was carried out using the methodology given in [15]. The essence of the method for determining the swelling coefficient is to expose a sample of a fire-retardant coating applied to a wooden substrate to a high-density heat flux and measure the formed layer of foam coke after it cools.

5. Results of determining the properties of a fire-retardant composition with the presence of biopolymers for fire protection of wood

5.1. Results of research into the process of forming a composite coating with the addition of biopolymers and its identification

Fig. 1 shows the IR spectra of the studied samples of a fire-retardant composition with the presence of biopolymers.

The samples that were analyzed have the same composition in different ratios of additives. The structure of the starch molecule is similar to the structure of the cellulose molecule, which is part of wood. The simplest formula of both molecules is $(C_6H_{10}O_5)_n$. In this formula, the value of n is from several hundred to several thousand. Starch and cellulose are natural polymers that consist of repeatedly repeating structural units $-C_6H_{10}O_5$. Compared to starch, cellulose has a higher relative molecular mass. The structural unit of starch and cellulose is the pyranose cycle. Coffee grounds contain 50% carbohydrates, 20–25% cellulose, 5–7% pentosans, and other substances. Pentosans are also part of the hemicellulose part of wood, which also contains lignin. The similarity of the components of additives added to the base coating is reflected in the similarity of the IR transmission spectra.

Analysis of the IR spectra from Fourier samples (1, 2, 3, 4) reveals the similarity of the transmission bands. The largest markers are the transmission bands in the wavelength range of 2400–3700 cm⁻¹. The transmission bands of the IR spectrum in the range of 3700–3100 cm⁻¹ characterize the stretching vibrations of different types of hydroxyl groups in lignin, in particular, the stretching vibrations of aliphatic hydroxyl groups, as well as the OH groups of cellulose, components of starch amylose and amylopectin and the

hemicellulose part (xylan, pentosan, etc.), components of coffee. All hydroxyl groups participate in hydrogen bonds. The region of 3000–2800 cm⁻¹ characterizes the symmetric and asymmetric C–H stretching vibrations in the methyl and methylene groups of lignin. Stretching vibrations of C–H bonds in methylene and methine groups appear in the region of 3000–2800 cm⁻¹. In xylan, pentosan, stretching vibrations of C–H groups CH₃, CH₂ and CH appear with a maximum at 2930 cm⁻¹.

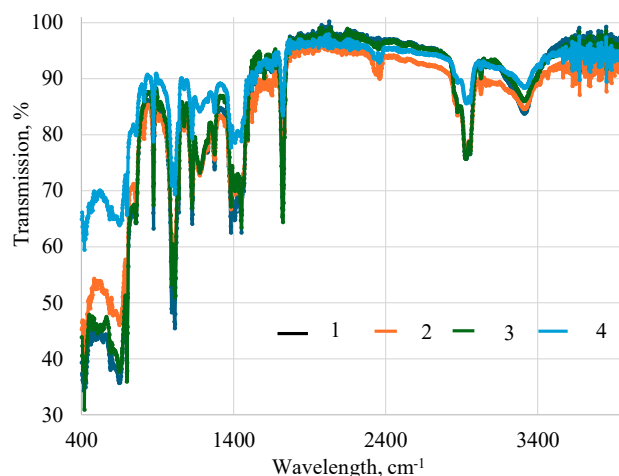


Fig. 1. Transmission spectra of samples: 1 – base coating and with the addition of: 2 – wood flour; 3 – starch; 4 – coffee grounds

Thus, a fire-retardant composition with the presence of biopolymers is an accumulation of biological substances with nitrogen-phosphorus flame retardants, carbohydrates, and gas-forming substances, surrounded by a polymer binder.

To establish the individual characteristics of the samples of the composition with a biopolymer, thermogravimetric analysis was performed. Graphic images of thermogravimetric analysis are shown in Fig. 2–5.

In all samples of the fire retardant composition at temperatures up to 100°C, endothermic processes occur, during which mass loss occurs due to evaporation of water without destruction of the materials of the fire retardant composition and wood and the release of gaseous volatile substances.

Endothermic effects within the temperature range of 180–200°C are associated with the fact that organic substances lose water with additional mass loss and decomposition of ammonium polyphosphate, rearrangement, and dehydration of melamine.

In the temperature range of 200–300°C, biopolymers begin to decompose, which are superimposed on the effect of pentaerythritol decomposition with the formation of ketones and aldehydes. Intensive nucleation of the pinocoke cell occurs. When melamine decomposition products interact with pentaerythritol aldehydes, methylol is formed, and then polymer-oligomeric structures of the amino resin.

At a temperature of approximately 300–370°C, intensive decomposition of ammonium polyphosphate into ammonia and polyphosphoric acid begins, which is confirmed by endothermic peaks (melting of crystal structures) that characterize polyphosphates. The beginning of intensive mass loss of the fire-retardant composition is characterized by a temperature of 320–330°C, when the sublimation peak of melamine is superimposed, which begins at a temperature

of 330°C and ends at a temperature above 420°C. This corresponds to intensive formation of foam coke (the relative mass loss reached 60–70%). Such a difference in the influence of biopolymers on the course of thermal destruction at different stages is due to certain mechanisms by which the mass loss of samples occurs.

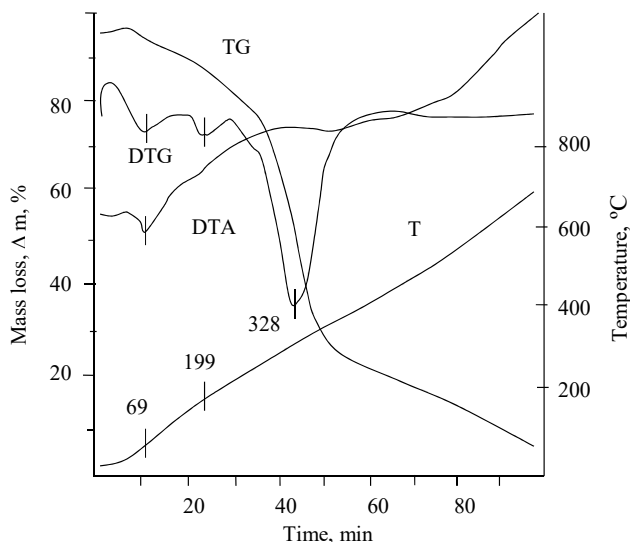


Fig. 2. Thermogravimetric analysis curves for a sample of a fire retardant composition: T – temperature curve; DT – mass loss curve depending on the temperature increase; DTA – thermal effects curve; DTG – differential curve

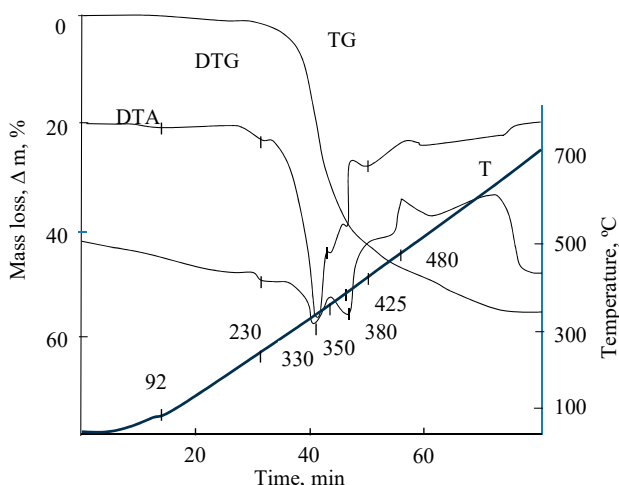


Fig. 3. Thermogravimetric analysis curves for a sample of a fire-retardant composition filled with wood flour: T – temperature curve; DT – mass loss curve depending on the temperature increase; DTA – thermal effects curve; DTG – differential curve

If at the first stage there is mainly pyrolysis with the cleavage of volatile products of biopolymers, the rate of which does not depend on the subsequent chemical transformations of these products. At the second stage, the rate of mass loss is determined by the kinetics of the interaction of the carbonized residue with the oxidant.

Thus, thermogravimetric studies have revealed that under the influence of thermal action, chemical reactions of the fire-retardant composition begin, including ammonium polyphosphate, which, when decomposed, releases phosphoric acid. That, in turn, affects the destruction of the biopolymer and the dehydration of pentaerythritol with the formation of

soot, and the simultaneous decomposition of melamine leads to the release of non-combustible gases, which cause the soot to foam and form foam coke.

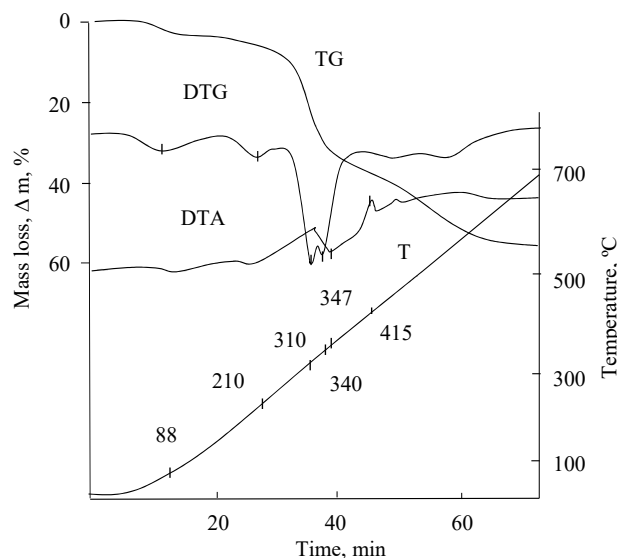


Fig. 4. Thermogravimetric analysis curves for a sample of a starch-filled fire retardant composition: T – temperature curve; DT – mass loss curve depending on temperature increase; DTA – thermal effects curve; DTG – differential curve

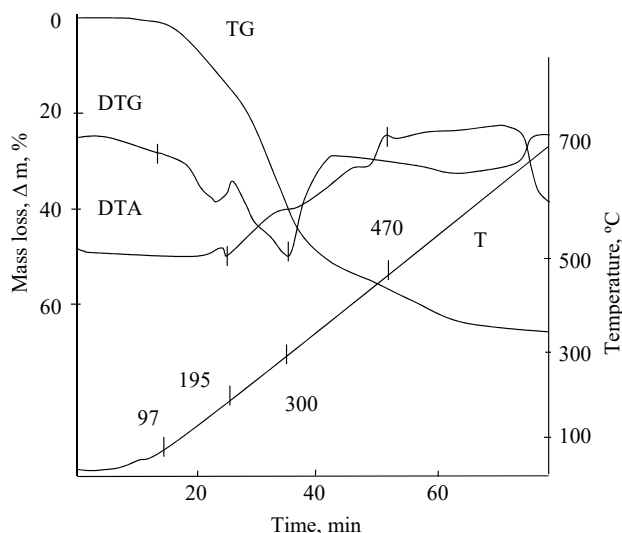


Fig. 5. Thermogravimetric analysis curves for a sample of a fire-retardant composition filled with coffee grounds: T – temperature curve; DT – mass loss curve depending on temperature increase; DTA – thermal effects curve; DTG – differential curve

5. 2. Results of studies on the formation of surface characteristics when adding biopolymers to the composite coating and changing the thermal insulation layer of foam coke

Fig. 6 shows the process of determining the surface tension of the fire-retardant composition with the presence of biopolymers.

Taking into account the initial values of the ring dimensions: outer diameter 12 mm and wire thickness 1.0 mm and tensiometer reading within 500–600 mg, the research results showed that the surface tension for the fire-retardant composition was 28.8 mJ/m².

The addition of biopolymers almost did not change the value of surface tension, namely, for the composition with the presence of wood flour it was 27.4 mJ/m^2 , with the presence of starch – 29.6 mJ/m^2 , with the presence of coffee grounds – 28.1 mJ/m^2 .

The wetting contact angle of the fire-retardant composition with the presence of biopolymers was determined on the samples of the test materials given in Table 1.

Testing: a drop of the fire-retardant composition with the presence of biopolymers was applied to the sample of the test material using a pipette (Fig. 7–10). After the drop reached an equilibrium state, its height and diameter were determined using a microscope with a certain degree of magnification.

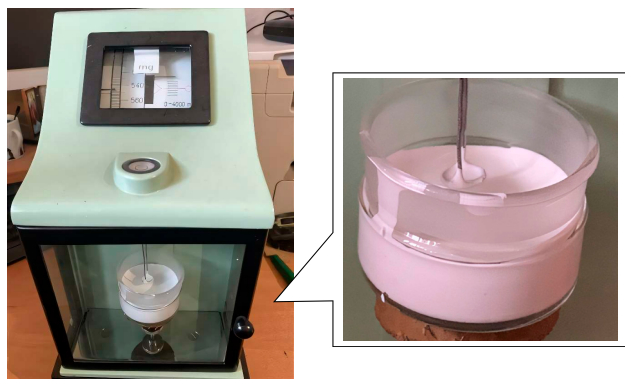


Fig. 6. Determining the surface tension of a flame retardant composition

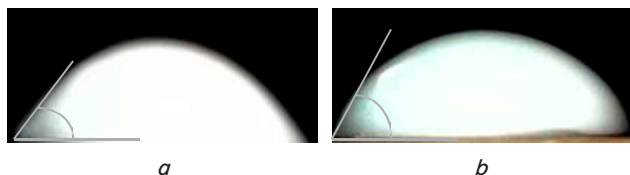


Fig. 7. A drop of fire retardant composition applied to the test material: *a* – glass; *b* – polyvinyl chloride

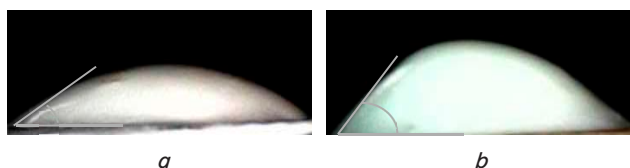


Fig. 8. A drop of fire retardant composition with wood flour applied to the test material: *a* – glass; *b* – polyvinyl chloride

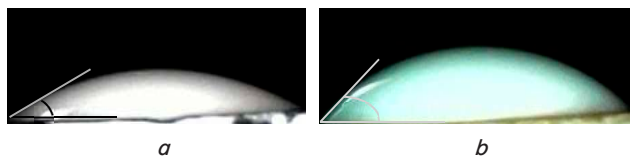


Fig. 9. A drop of a fire-retardant composition with starch applied to the test material: *a* – glass; *b* – polyvinyl chloride

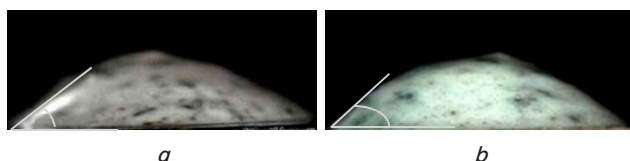


Fig. 10. A drop of fire retardant composition with coffee grounds applied to the test material:
a – glass; *b* – polyvinyl chloride

The above results (Fig. 7–10) show that the fire retardant composition when wetting glass forms an angle of about 55° , and polyvinyl chloride – 62° . When wetting with a fire retardant composition with the presence of biopolymers of glass and polyvinyl chloride, the wetting angle decreases.

The results of determining the contact angle of wetting by a fire retardant composition with the presence of biopolymers of test materials and determining the corresponding components of the free energy of the surface are given in Table 2.

The results of determining the corresponding components of the free energy of the surface of pine wood showed that the polar component is 8.2 mJ/m^2 , the dispersed component is 41.4 mJ/m^2 , and the polarity is 16.5. The polarity of the fire-retardant composition with the presence of biopolymers exceeds the value of wood by three times and shows that the above composition and with the addition of biopolymers will effectively cover wood. Fig. 11 shows the treated samples of pine wood.

Table 2

Wetting contact angle and free energy component of the surface of a flame retardant composition with the presence of biopolymers

Composition with the addition of biopolymer	Edge wetting angle, $\theta,^\circ$		Free surface energy, mJ/m^2			Polarity, %
	Glass	Polyvinyl chloride	General	Polar	Dispersed	
–	55	62	28.8	17.1	11.7	59.3
Wood flour	40	55	27.4	14.8	12.6	54.0
Starch	31	50	29.6	16.9	12.7	57.1
Coffee grounds	38	42	28.1	17.4	10.7	61.9

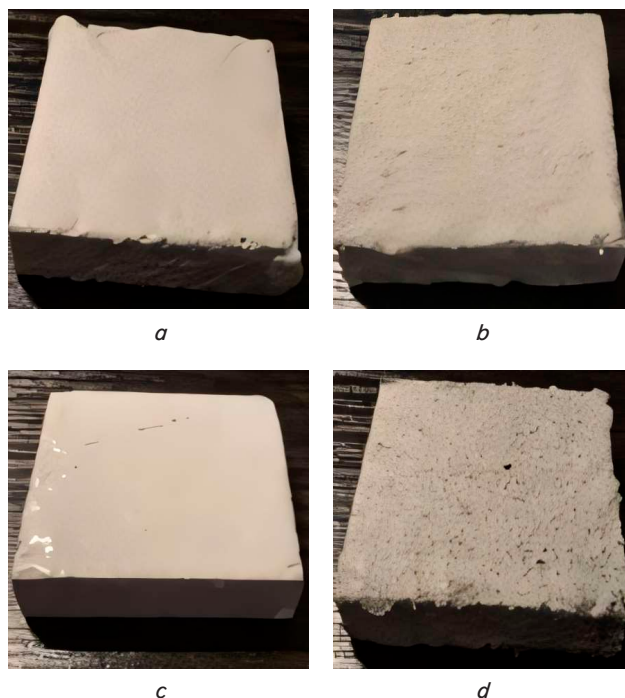


Fig. 11. Pine wood samples treated with a fire-retardant composition containing biopolymers: *a* – basic composition; *b* – with the addition of wood flour; *c* – with the addition of starch; *d* – with the addition of coffee grounds

After examining the relationship between wood and a fire retardant composition with the presence of biopolymers, a study was conducted to determine the swelling coefficient.

Fig. 12, Table 3 show the results of studies on the swelling process of a fire retardant composition with the presence of biopolymers.

As can be seen from Fig. 12, under the action of the radiation panel, the flame retardant composition of all experimental samples swelled. Thus, for the base sample, the swelling is associated with the decomposition of flame retardants under the influence of temperature. For samples of the flame retardant composition with the presence of biopolymers, swelling was recorded, exceeding the base, despite the smaller amount of flame retardants.

When the radiation panel acted on the fireproof composition, swelling and formation of a thermal insulation layer of foam coke occurred. For the base sample, the swelling time was recorded for 102 s, which then increased by about 1.25 times. This is due to a decrease in the amount of flame retardants due to the addition of biopolymers, which increased the foam coke layer. Thus, when adding coffee grounds, the height of the coke layer increased to 12.5 mm, for biopolymers such as wood flour and starch, the coke height increased by more than 15 mm, and the foam multiplicity increased by 1.2 times.

Table 3

Determining foam multiplicity during swelling of a fire-retardant composition with the presence of biopolymers under thermal influence

Composition with the addition of biopolymer	Swelling time, s	Flue gas temperature, °C	Coating thickness, mm	Coke layer height, mm	Foam multiplicity, score
–	102	71	0.52	13.0	25.0
Wood flour	125	78	0.56	15.3	27.3
Starch	128	82	0.57	15.4	27.0
Coffee grounds	122	86	0.54	12.5	23.1

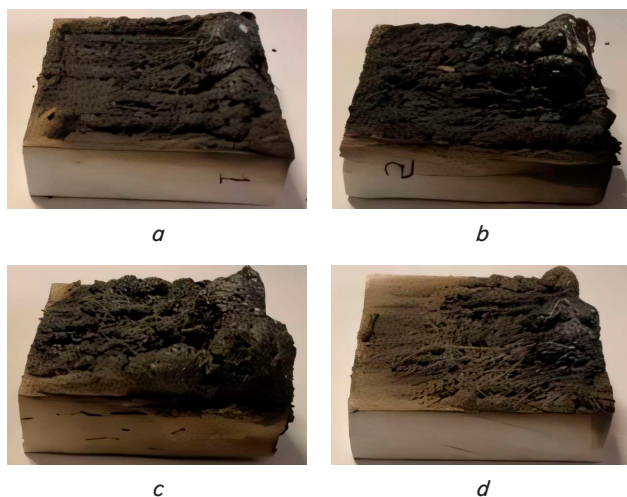


Fig. 12. Results of research on the swelling process: *a* – base sample; *b* – base sample with the addition of wood flour; *c* – base sample with the addition of starch; *d* – base sample with the addition of coffee grounds

6. Discussion of results based on studying the regularities of fire protection of wood by composite coating with biopolymer

The results of studies on the structure of the fire-retardant composition filled with biopolymers showed that they

represent an accumulation of biological substances with nitrogen-phosphorus flame retardants, carbohydrates, and gas-forming substances in the polymer matrix, as indicated by the transmission spectra (Fig. 1). Under the influence of thermal action on the fire-retardant compositions, chemical reactions begin (Fig. 2–5), including ammonium polyphosphate, which, upon decomposition, releases phosphoric acid. That, in turn, affects the destruction of the biopolymer and the dehydration of pentaerythritol with the formation of soot, and the simultaneous decomposition of melamine leads to the release of non-combustible gases, which cause the soot to foam and form foam coke.

According to the results of studies on the surface energy characteristics of the fire-retardant composition with the presence of biopolymers, it was found that the surface tension for the basic fire-retardant composition (Fig. 6) was 28.8 mJ/m². The addition of biopolymers almost did not change the value of the surface tension, for the composition with the presence of wood flour it was 27.4 mJ/m², with the presence of starch – 29.6 mJ/m², with the presence of coffee grounds – 28.1 mJ/m². The contact angle of the fire-retardant composition with the presence of biopolymers on the test material samples shows that the fire-retardant composition when wetting glass forms an angle of about 55°, and polyvinyl chloride – 62°. When adding biopolymers to the fire-retardant composition, the contact angle decreases. Considering that the polarity of wood is 16.5%, the polarity of the fire retardant composition with the presence of biopolymers exceeds the value of untreated wood by 3.5 times. This confirms that the above composition and with the addition of biopolymers will effectively cover wood [16, 17]. As can be seen from Fig. 6, under the action of the radiation panel, the fire retardant composition of all experimental samples swelled. For the base sample, the swelling time was recorded for 102 s, which then increased by about 1.25 times, which is associated with a decrease in the amount of flame retardants by adding biopolymers, which in turn affected the increase in the foam coke layer. Thus, when coffee grounds were added, the coke layer height increased to 12.5 mm, for biopolymers such as wood flour and starch, the coke height increased to over 15 mm, and the foam multiplicity increased by 1.2 times. This reflects the participation of biopolymers in the formation of the foam coke layer, which can be identified directly by high-temperature exposure to samples of the fire-retardant composition [18, 19].

Unlike the studies reported in [4, 5, 8], in which the attention was paid to coatings based on biocomposites, our study considered a fire-retardant composition, which is quite well-known in the market.

However, unlike the results obtained in [3] regarding the mechanism of fire protection, the following can be stated:

- the main regularity of high-temperature inhibition of wood is only the release of water vapor, which affects the flame, and the formation of a ceramic phase, which is inherent in geocement coatings;

- the mechanism of operation of the fire-retardant composition is that under the influence of thermal action, chemical reactions begin in the fire-retardant composition, including ammonium polyphosphate, which affects the destruction of the biopolymer and the dehydration of pentaerythritol with the formation of soot, and the simultaneous decomposition of melamine leads to the release of non-combustible gases, which cause the soot to foam and form foam coke.

This representation of our results, since the fire-retardant composition was confirmed by the reaction to the action of a

high-temperature flame, shows the real aspects of operation. The results of the experiments showed that the fire-retardant composition has the potential, which is manifested in the formation of a heat-insulating layer of coke, and the establishment of the swelling multiplicity shows how the biopolymer affects the formation of hydrocarbons.

The results obtained on the free energy of the surface of the fire-retardant composition have certain limitations when determining the components due to the unpredictability of the process of the contact angle during wetting, taking into account which is possible provided that the surface properties of the coating layer are ensured, which is formed during wood processing.

In addition, the resistance of the fire-retardant composition to thermal effects does not provide sufficiently informative indicators due to the scarcity of these ones relative to the foam coke layer and limits the use of our results. The disadvantage of the experimental method used is the complexity, which limits the determination of the swelling effect. However, owing to fire experiments, it is possible to obtain results that make it possible to establish the role of biopolymers in the formation of the coke layer. Further development of our research into the formation of biocomposites for fire protection of wood-polymer products may initiate future studies, in particular to optimize experimental data on formulation design.

7. Conclusions

1. A fire retardant composition with the presence of biopolymers is an accumulation of biological substances with nitrogen-phosphorus flame retardants, carbohydrates, and gas-forming substances, bound by a polymer binder. Thermogravimetric studies have shown that under the influence of thermal action, chemical reactions begin in the fire retardant composition, such as the decomposition of ammonium polyphosphate, which releases phosphoric acid. This leads to the destruction of the biopolymer and the dehydration of pentaerythritol with the formation of a large number of hydrocarbons, and the simultaneous decomposition of melamine leads to the release of non-combustible gases, which cause the soot to foam and form foam coke.
2. The surface energy characteristics of the fire retardant composition with the presence of biopolymers have been studied and it was found that the surface tension for the basic fire retardant composition was 28.8 mJ/m². The addition of biopolymers to the fire retardant composition did not change the surface tension value, but the wetting angle

decreases. Considering that the polarity of wood is 16.5%, the polarity of the fire retardant composition with the presence of biopolymers exceeds the value of untreated wood by 3.5 times, which provides effective treatment of the wood surface. According to the results of the thermal effect on the samples, it was found that swelling of the fire retardant composition occurred under the action of the radiation panel. Thus, for the basic sample of the fire retardant composition, the swelling time was recorded for 102 s, which then increased by about 12.5 times. When coffee grounds were added to the composition, the height of the coke layer increased to 12.5 mm; when biopolymers such as wood flour and starch were added, the coke height increased to over 15 mm, and the foam multiplicity increased by 1.2 times.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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