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Intensification of the formation process of sodium sulfate-modified biocomposite materials based on the glutinous matrix

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The influence of a modifying additive (sodium sulfate) on the regime of heat treatment of the biocomposition in a mold was studied. The optimal content of sodium sulfate in the biocomposite material was determined. The influence of the content of the modifying additive on the compressive strength of biocomposites structured at different temperatures was studied. The optimal parameters of the thermal field temperature and the duration of heat treatment of the biocomposite for a given content of the additive, which provide the maximum values of mechanical characteristics, are determined. It was established that the modifying additive with an optimal content contributes to an increase in the intensity of structuring of the biopolymer binder. This is manifested in the rapid transition of the glutin binder from the gel-like state to the solid state with the formation of physicochemical bonds due to the removal of excess moisture under the influence of temperature. Fractograms of the fracture surface of the biocomposites containing sodium sulfate are analyzed.

Keywords: biocomposite, glutin binder, wood flour, sodium sulfate, heat treatment, compressive strength.

Інтенсифікація процесу формування модифікованих сульфатом натрію біокомпозитних матеріалів на основі глютинової матриці. *В.П.Кашицький, О.Л.Садова, С.Л.Янчук*

В статті досліджено вплив модифікуючої добавки (сульфату натрію) на режим термічної обробки біокомпозиції у прес-формі. Визначено оптимальний вміст сульфату натрію в біокомпозитному матеріалі. Досліджено вплив вмісту модифікуючої добавки на межу міцності на стиск біокомпозитів, структурованих за різних температур. Визначено оптимальні параметри температури теплового поля та витримки під час термічної обробки біокомпозиції для заданого вмісту добавки, яка забезпечує максимальні значення механічних характеристик. Встановлено, що модифікуюча добавка за оптимального вмісту здатна підвищувати інтенсивність формування біополімерного в'яжучого, що полягає у швидкому переході глютинового в'яжучого з гелеподібного стану у твердий з утворенням фізико-хімічних зв'язків за рахунок видалення надлишкової вологи під впливом температури. Проаналізовано фрактограми зламу поверхні біокомпозитів з вмістом сульфату натрію.

1. Introduction

At present, biocomposite materials based on natural components are widely used for the manufacture of structural parts, as they have high values of physical, mechanical and operational characteristics. These materials are eco-friendly during the molding process. Biocomposites do not harm the environment if they end up in landfills. The raw material for the production of biocomposites belongs to renewable sources, which provides stability in the extraction of components and the ability to obtain unlimited raw materials. However, there are technological problems associated with the duration of the formation of biocomposite products. There are difficulties with the removal of excess moisture, which requires increasing the duration of the thermal field. Therefore, scientific interest is the study of the influence of modifying additives on the intensification of the structuring process of the biopolymer matrix, determining the physical and mechanical characteristics and studying the structure of the developed biocomposite materials [1, 2].

Biopolymers are obtained from natural resources. Biopolymers consist of monomeric units that are covalently bonded to form larger structures. Biopolymers differ in melt fluidity, resistance to dynamic loads, hardness, vapor permeability, friction coefficient and decomposition coefficient. Biopolymers can be thermosetting, thermoplastic and elastomeric. Biopolymers have a wide range of applications in various industries, such as agricultural films, automotive, medical and pharmaceutical, food packaging, hygiene and protective clothing [3–5].

There are many different types of biodegradable matrices for the production of biocomposites. The main obstacle to greater commercialization of eco-friendly composites is their relatively high price. Successful development of each type of biomatrix, regardless of their biodegradability, is a complex task. It is necessary to take into account the origin of raw materials, energy spent on the transformation of the original matrix of raw materials, and assessment of the life cycle of bioplastics from production to processing, taking into account design and engineering work to create matrices [6]. The most available source of raw materials for the production of biomatrices are starch and cellulose. Cellulose, isolated from wood and cotton processing residues, is suitable for bioplastic production. Starch is a relatively convenient raw material for creating a biomatrix. Unlike cellulosic plastic, starch biomatrices have a greater degree of biodegradability and poorer physical and mechanical properties [7]. A typical process of creating biomatrices mostly involves the decomposition of the main macromolecules of raw materials and the connection of different types of side chains with the main chain in order to redistribute atoms and molecules by activating the polymerization of raw materials.

Biopolymers are produced from natural and renewable raw materials. Examples of such polymeric materials are thermoplastic starch, polyhydroxyalkanoates (PHA), polylactides (PLA), lignin-based epoxy resin, soy-based resin and epoxy linseed oil [8]. Despite the fact that there are a large number of different types of bio-based polymeric materials, the development of eco-friendly sector of the chemical industry is based on the production of biodegradable plastics. Biodegradable plastics and biopolymer materials made from renewable raw materials are the basis of an eco-product that is increasingly replacing products made from synthetic polymer materials, that is petrochemical products [8, 9].

A composite material is considered a biocomposite in the case of combined use of biomatrix with natural fillers and additives. Thus, all components must be of natural origin. This is sometimes quite difficult to achieve in the case of using modifying additives that increase the mechanical properties of the composite [4].

Along with the advantages of biopolymers and natural fillers, there are many problems, the solution of which would provide improved physical, mechanical and operational characteristics of biocomposites. Therefore, attention is focused on the physical and chemical modification of the surface of fillers to increase their adhesion to the matrix [7].

The direct consequence of water absorption is the structural changes of the biocomposite, its shrinkage and swelling, which is especially observed in composites with a high content of filler. The absorption of moisture and water occurs directly on the surface of the wood filler, which leads to a decrease in hydrogen bonds and a deterioration in the mechanical properties of the composite. For this reason, moisture (water) must be removed from the filler particles before mixing them with the matrix. Increasing the initial moisture content in the filler increases the likelihood of the formation of potentially undesirable compounds. These reduce the density, increase the porosity and water absorption of composites. This disadvantage is partially offset by a decrease in the filler content in the total mass of the biocomposite. Although the hygroscopicity of wood filler is an important technical problem, it can be solved by one of the types of treatment of filler particles: high-temperature drying of filler particles, acetylation of biofibers and surface grafting [9, 10].

Physical and mechanical properties and fire resistance of natural fillers can be improved by processing them. Moisture absorption can be reduced by modifying the surface and adding hydrophobic substances.

Adhesion between the natural filler and the polymer matrix in the composite is considered to be the main factor for obtaining high mechanical properties of the fiber-reinforced composite. An important requirement for high adhesion of fibers to the matrix is the optimizing impregnation of the reinforcing system. The presence of hydroxyl and polar groups in natural plant fillers leads to high absorption of moisture by plant fiber. This results in a weak interfacial bond between the natural filler and the polymer of the hydrophobic matrix. Obtaining a strong bond between the natural filler and the polymer is problematic due to the different chemical structure of the fillers and the matrix. This leads to inefficient stress transfer at the interface of the obtained composites. Chemical modification of fillers is performed to reduce their hydrophilic capacity and moisture absorption, which increases the mechanical characteristics of biocomposites [11–13]. Many attempts have been made to modify the surface of natural fibers to increase their adhesion to the matrix by acetylation, acrylation, alkaline processing, benzoylation, corona treatment, graft copolymerization, heat treatment, plasma treatment, silane treatment, stearic acid treatment and other chemical modifications [14–16]. Surface chemical modification of natural fibers slightly improves their adhesion to the polymer. Finishing agents are also used in composite materials to improve the chemical bond between dissimilar materials. Finishing agents perform the function of an intermediate material between the polymer and natural fillers and improve their adhesion [17, 18].

The main objectives of the work were: to optimize the mode of heat treatment and the content of the modifying additive; to determine the influence of temperature and endurance in the thermal field on the compressive strength of biocomposites based on glutin (bone glue) and wood flour; to study the microstructure of developed biocomposite materials.

2. Experimental

The compressive strength of biocomposite samples was determined by ASTM D695. Cylindrical specimens with a diameter of 20±0.5 mm and a height of 30 mm were subjected to compression at a uniformly increasing load at a speed of approaching the press traverse of 2 mm/min.

The investigation of the surface structure of biocomposites and the detailed study of individual areas of the surface at high magnifications was performed on a scanning electron microscope (Zeiss Leo Supra 35) at the magnification (×100) and an accelerating voltage of 15 kV.

The samples were prepared using an aqueous solution of bone glue (glutin) and wood flour, which were mixed to obtain a homogeneous mixture. Glutin was dissolved in water for 3 *h* at a temperature of 50°C with the calculated ratio of components. The composition was prepared by mechanically mixing of the solution of glutin with wood flour. Subsequently, the composition was placed in a mold and subjected to compression (5–6 MPa). Then the mold was placed in a drying chamber, where heat treatment (HT1) was carried out in the temperature range of 130–170°C. The product was removed after cooling the mold to a temperature of 18–20°C.

In the first stage, the heat treatment of the composition in the mold should be carried out in a stepwise mode with heating to a given temperature for one hour, followed by application of additional pressure and continued heating to the temperature at which the precomposition was maintained in the first stage of heat treatment. The binder is heated gradually with increasing solubility of bone glue, which leads to wetting of wood flour particles and the formation of chemical bonds between the components. The additional pressure ensures the compaction of the press composition, since during heat treatment moisture is removed and cavities are formed, which reduce the strength of the biocomposite product.

IR-spectrogramme recorded on a spectrophotometer IRAffinity-1S in the frequency range 400-4000 cm^{-1} by a single-beam method in reflected light. Infrared spectrograms processed by IRSolution computer program.

3. Results

The biocomposition is prepared by combining a solution of bone glue with wood flour, followed by mechanical mixing of the mixture to ensure homogeneity and saturation of the surface of the particles with a solution of bone glue. Biocomposite materials are formed on the basis of biopolymer binder and wood flour by pressing the composition in the form, followed by heating to melt the gluten. Heat treatment is carried out in a closed mold under pressure to ensure the homogeneity of the product, because under the influence of high temperature (more than 100°C) intense evaporation of moisture occurs. Heat treatment allows evenly filling the interparticle space with biopolymer binders and forming physico-chemical bonds between the particles of wood flour. The duration of heat treatment is determined by the need to ensure complete structuring of the system and the removal of moisture, which reduces the strength of biocomposite materials. In the presence of moisture in the material, the resistance of the material layers to displacement under the action of an external load decreases. The heat treatment of the composition takes place in a closed mold, so the removal of moisture is difficult; this fact increases the duration of heat treatment. In the technological process, this leads to an increase in the cost of biocomposite products, since the number of products in the batch decreases and energy costs increase. To solve the problem, it is necessary to use modifying additives that can intensify the structuring process by increasing the rate of formation of physico-chemical bonds and removal of moisture.

It is known that the introduction of sulfate ions into the bone glue solution leads to an increase in the rate of transition of the solution to the solid state, which has a positive effect on the process of structuring the biocomposite material. The most common sulfate is sodium sulfate (Na_2SO_4), which is commercially available, environmentally friendly and inexpensive. The main task is to determine the optimal content of sodium sulfate, which affects the heat treatment of the composition in the mold. The mode of heat treatment is determined by two main parameters: temperature and duration of exposure. The mode of heat treatment can vary with different content of sodium sulfate. Therefore, it is necessary to determine the optimal heat treatment parameters for a given content of the additive, which will provide the maximum values of mechanical characteristics.

Theoretical calculations for the search for optimal values require practical confirmation by conducting experimental studies. Elevated temperature leads to the destruction of the biopolymer binder. Therefore, heat treatment of biocomposite materials without a mold should be carried out at a temperature of 130°C in the range of sodium sulfate content of 17–116 parts by weight. The increase in compressive strength occurs within up to 83 parts by weight, which is due to the optimal content of the biopolymer matrix (Fig. 1). This ensures the adsorption of the glutin macromolecules on the surface of wood flour particles, resulting in the formation of physico-chemical bonds. At a higher binder content (83–116 parts by weight) there is a decrease in compressive strength due to an increase in the thickness of the interparticle layers, which are subjected to plastic deformation under mechanical stress. This leads to a shift of the local volumes of the sample and the formation of barrel-shaped samples, which indicates the dominance of the plastic type of deformation.

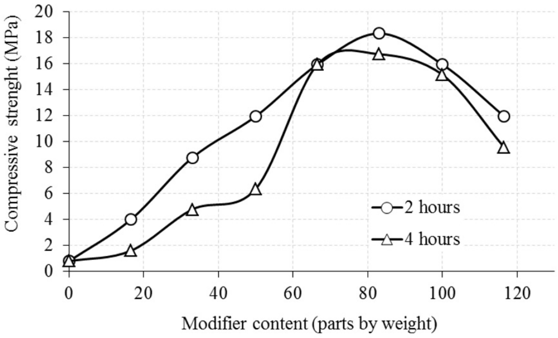


Fig. 1. Influence of modifier content on compressive strength of biocomposites structured at 130°C.

Higher values of compressive strength were obtained in the case of exposure samples for 2 *h* compared to exposure for 4 hours. At the higher exposure, there is a destruction of surface layers of biocomposite material, which is in direct contact with the heated inner surface of the mold. The shorter exposure time is more advantageous in the technological process of manufacturing biocomposite products, as it provides an increase in the production program and reduce energy costs.

A significant increase in compressive strength of biocomposites structured at a temperature of 150°C does not occur in the case of sodium sulfate content up to 50 parts by weight (Fig. 2). However, when the content of the modifying additive is 60–80 parts by weight, the compressive strength increases by 75–88 %. This is due to the uniform distribution of the biopolymer binder in the volume of the sample due to the melting of the solution at a temperature of 150°C and the optimal content of sodium sulfate. The modifying additive at the optimal content increases the rate of solidification of the biopolymer binder, i.e. there is an intensive transition of glutin from a gel-like to a solid state with the

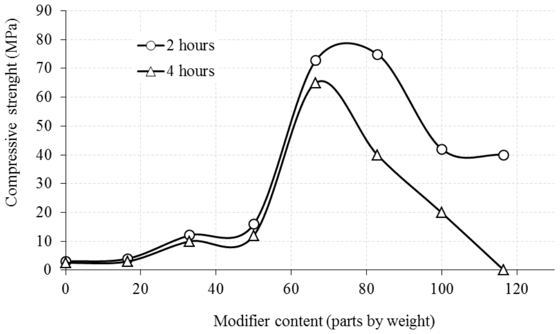


Fig. 2. Influence of modifier content on compressive strength of biocomposites structured at 150°C.

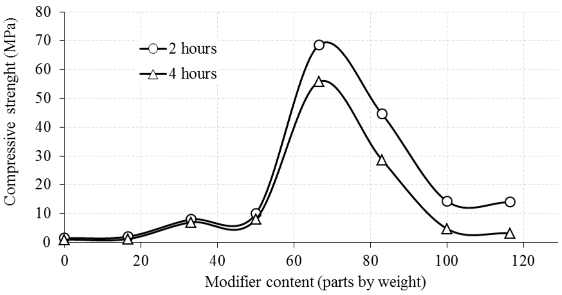


Fig. 3. Influence of modifier content on compressive strength of biocomposites structured at 170°C.

formation of physico-chemical bonds by removing excess moisture under the influence of temperature.

The increased content of sodium sulfate leads to a significant decrease in compressive strength, since the excess content of the modifying additive causes local structuring of the volumes of the biocomposite sample without uniform distribution of the biopolymer binder. This leads to the appearance of concentrators of stresses and inhomogeneities of the structure, which reduce the strength of the biocomposite material.

In the case of exposure for 4 *h* in the drying chamber, biocomposite samples with a sodium sulfate content of up to 70 parts by weight do not have significant changes in the compressive strength. This indicates the insufficient effect of the modifying additive on the structure-forming processes. In biocomposites with a content of sodium sulfate 70–116 parts by weight there is a decrease in the compressive strength by 30–35 %. Increased exposure leads to the fact that the biocomposite receives more thermal energy, which causes the destruction of the surface layers of the biocomposite sample.

Increasing the heat treatment temperature to 170°C reduces the compressive strength of biocomposites by 10–13 % compared to the treatment temperature of 150°C. This is due to the intensification of structuring processes at higher temperatures and uneven distribution of biopolymer binder, which leads to the simultaneous process of structuring and destruction of the biopolymer matrix. The heat treatment with an exposure for 4 *h* leads to a decrease in the compressive strength in the case of using a modifying additive above 70 parts by weight, due to excess heat energy received by the biocomposite material. Accordingly, it causes the formation of a structure with high stress, which reduces the strength of biocomposites.

The microstructure of the biocomposite material that does not contain a modifying additive, has a low density, which is associated with the removal of moisture from the volume of the material during heat treatment (Fig. 4a). The destruction of biocomposites occurs at low loads due to the presence of exfoliation. On the surface of the biocomposite material there are oval inclusions, which are oriented at different angles (Fig. 4b). This is due to the presence of sodium sulfate crystals, which dissolve in the biopolymer matrix and cause anisotropy of local volumes. As a result, we get a small increase in strength, because the propagation of the crack is complicated by changing the direction of propagation. The introduction of sodium sulfate in the amount of 83 parts by weight leads to complete dissolution of the modifying additive. As a result, local volumes with high density occur (Fig. 4c), since sodium sulfate removes moisture from the cells of the gel-like glutin structure and intensifies the curing process of the biopolymer matrix. Such volumes have a higher strength compared to the biopolymer matrix that does not contain sodium sulfate, which provides intensive formation of a homogeneous structure.

On the surface of the fracture, there are particles of sodium sulfate, which did not dissolve in the biopolymer matrix due to the limited solubility of the modifying additive in the aqueous solution of bone glue (Fig. 4d). These particles do not form physicochemical bonds with the biopolymer matrix, since no wetting of the surface of the modifying additive with the binder was recorded. Accordingly, there is a decrease in compressive strength of biocomposites due to the absence of adhesive bonds and free movement of particles in the biopolymer matrix.

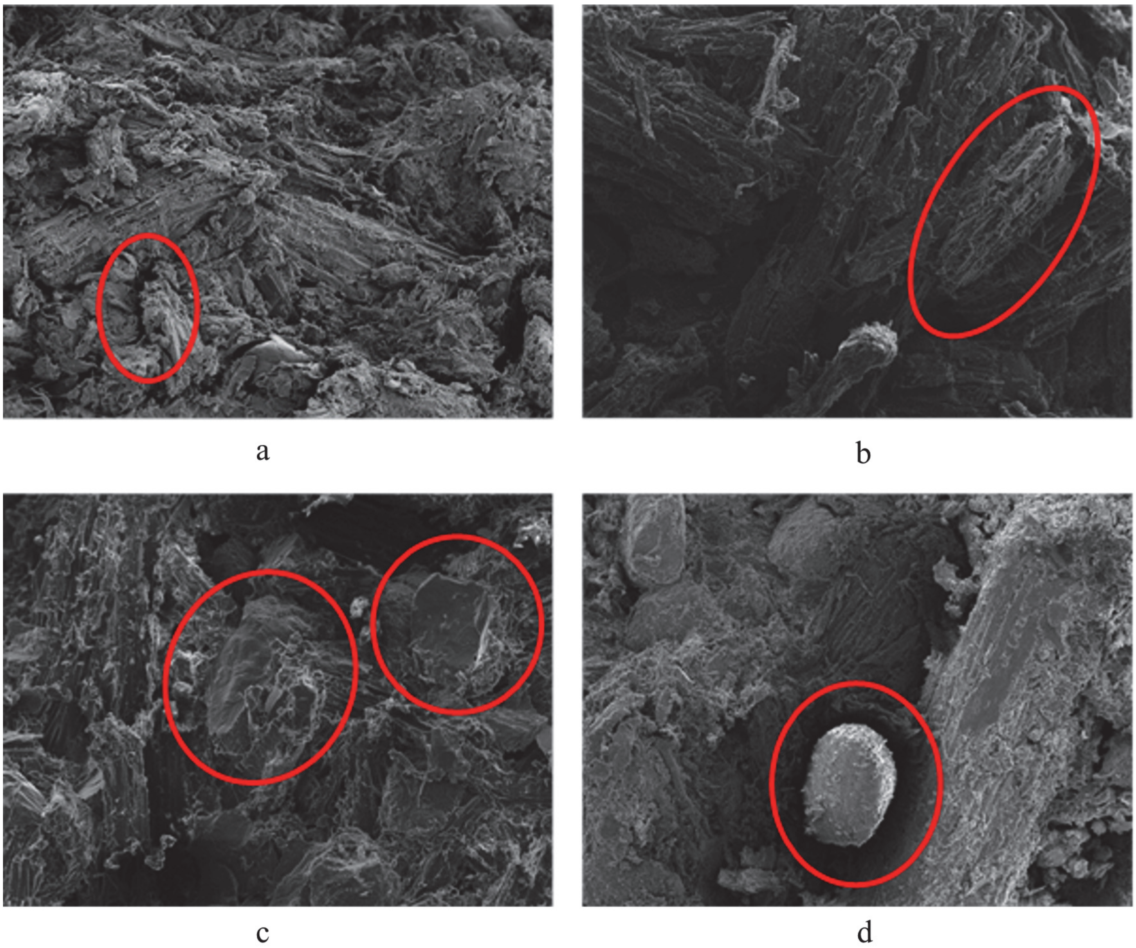
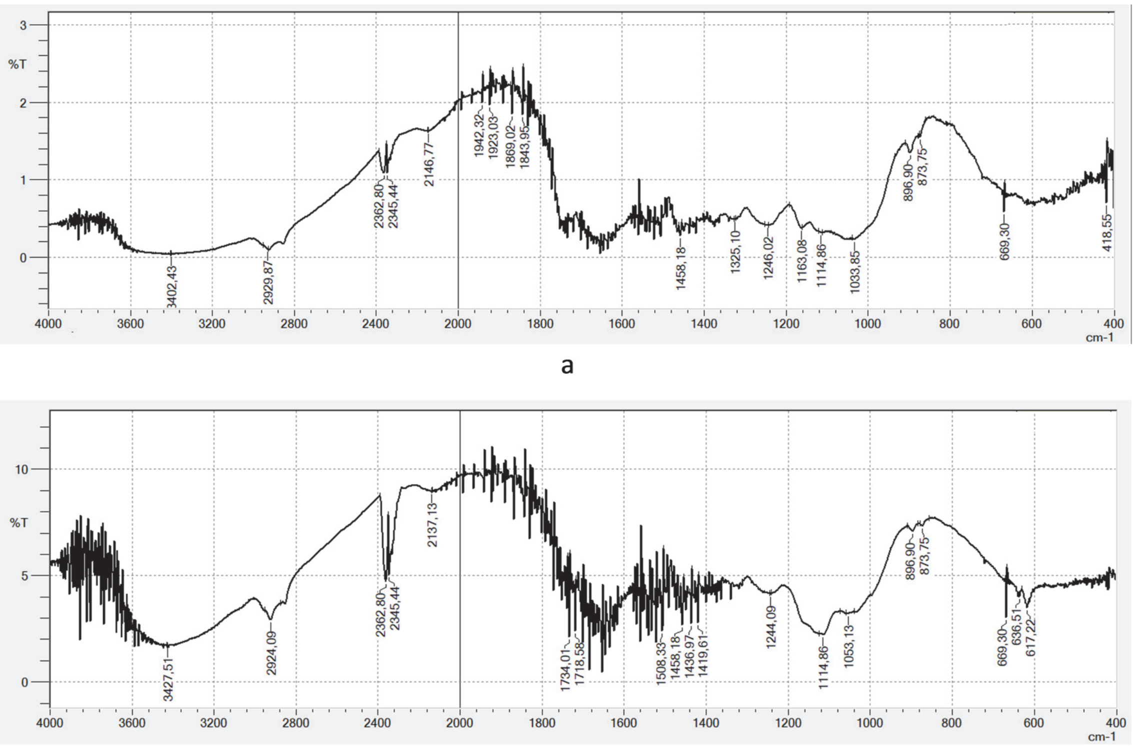


Fig. 4. Fractograms of fracture of the surface of biocomposites containing sodium sulfate: *a* – 17 parts by weight; *b* – 50 parts by weight; *c* – 83 parts by weight; *d* – 133 parts by weight.

On the IR-spectrum (Fig. 5) of the biocomposite, which does not contain a modifier, in the region of deformation and valence vibrations of simple bonds, an absorption band at a wave number ν = 669.30 cm^{-1} with an optical density D = 0.59 % and the peak area S = 3.83 % is revealed. The biocomposite containing the sodium sulfate modifier has additional absorption bands (Fig. 5b) at the wave number ν = 617.22 cm^{-1} with optical density D = 3.48 % and peak area S = 14.83 % and the wave number ν = 636.51 cm^{-1} with optical density D = 4.03 % and peak area S = 7.39 %. Also on the IR-spectrum of this biocomposite, a similar absorption band at the wave number ν = 669.30 cm^{-1}, but with a higher optical density D = 3.02 % and a smaller peak area S = 3.70 % was recorded. This indicates the presence of unreacted functional groups in this composite. For biocomposites without modifier, absorption bands were found at wave numbers ν = 873.75 cm^{-1} and ν = = 896.90cm^{-1} with optical densities D = 1.55 % and D = 1.35 %, respectively. For biocomposites containing a modifier, higher optical densities (D = 7.33 % and D = 7.11 %) and peak areas (S = 21.40 % and S = 25.04 %) were recorded for these wave numbers, that indicates the higher structuring of the biopolymer system.

For biocomposites that do not contain a modifier, absorption bands were recorded at wave numbers ν = 1033.85 cm^{-1} (optical density D = 0.23 %, peak area S = 103.55 %) and ν = 1246.02 cm^{-1} (optical density D = 0.41 %, peak area S = 7.68 %). Similar absorption bands, but shifted to the region of larger wave numbers, were found for biocomposites modified with sodium sulfate (ν = 1053.13 cm^{-1} with optical density D = 3.22 % and peak area S = 18.70 % and ν = 1244.09 cm^{-1} with optical density D = 4.14 % and peak area



a

b

Fig. 5. IR-spectrograms of biocomposites without modifier (a) and with modifier (sodium sulfate) (b)

S = 3.70 %). At the wave number ν = 1114.86 cm^{-1}, for biocomposites without modifier and with modifier, optical densities D = 0.32 % and D = 2.24 % and peak areas S = 7.69 % and S = 48.75 %, respectively, were recorded.

In the region of valence vibrations of multiple bonds (1500–2500 cm^{-1}) (C = C, C = O, C = N) for biocomposites, a complex spectrum of absorption bands was observed. For biocomposites without modifier, the absorption bands were recorded at wave numbers ν = 2146.77 cm^{-1} (D = 1.63 %, S = 3.79 %), ν = 2345.44 cm^{-1} (D = 1.09 %, S = 15.23 %), ν = 2362.80 cm^{-1} (D = 1.09 %, S = 38.11 %). Biocomposites modified with sodium sulfate have absorption bands at wave numbers ν = 2137.13 cm^{-1} (D = 8.96 %, S = 5.27 %), ν = 2345.44 cm^{-1} (D = 5.06 %, S = 5.44 %), ν = 2362.80 cm^{-1} (D = 4.73 %, S = 39.68 %). The biocomposite with sodium sulfate is characterized by higher optical densities and smaller peak areas at the same wave numbers that indicates a more complete structuring of the biopolymer matrix compared to the sample without a modifier.

For biocomposites without a modifier, absorption bands were recorded at wave numbers ν = 2929.87 cm^{-1} with optical density D = 0.11 % and peak area S = 25.04 % and ν = 3402.43 cm^{-1} with optical density D = 0.04 % and the peak area S = 5.78 %. The absorption bands are shifted to the lower frequency range for biocomposites modified with sodium sulfate (ν = 2924.09 cm^{-1} with optical density D = 2.92 % and peak area S = 74.59 %, ν = 3427.51 cm^{-1} with optical density D = 1.71 % and peak area S = 3.79 %). This informs about the influence of the modifier on the activation of the processes of formation of chemical bonds of the biopolymer matrix, which improves the structuring of the biocomposite material.

4. Conclusions

1. The compressive strength of biocomposites containing sodium sulfate in the amount of 60–80 parts by weight increases by 75–88 % in the case of processing samples at a temperature of 150°C. This is due to the uniform distribution of the biopolymer binder in the sample volume due to the melting of the solution under the influence of temperature and the optimal content

of sodium sulfate. The modifying additive with optimal content increases the rate of solidification of the biopolymer binder; there is an intensive transition of glutin from the gel-like state to the solid state with the formation of physico-chemical bonds by removing excess moisture under the influence of temperature. At the higher content of the binder (83–116 parts by weight) the compressive strength decreases, as the thickness of the interparticle layers increases, which are subjected to plastic deformation under mechanical stress.

2. It has been established that the introduction of sodium sulfate intensifies the process of structuring biocomposites; this leads to an increase in the compressive strength in the case of exposure to thermal field for 2 hours compared to exposure for 4 hours.

3. On the fracture surface of biocomposites with an optimal content of sodium sulfate in the amount of 83 parts by weight, the formation of local volumes with a high density was recorded. The modifying additive removes moisture from the cells of the gel-like structure of the glutin solution and intensifies the curing process of the biopolymer matrix. Additionly, these local inclusions have a higher strength compared to the biopolymer matrix without sodium sulfate, which provides the intensive formation of a homogeneous structure.

4. IR-spectroscopy confirmed that the biocomposite containing sodium sulfate is characterized by a more complete crosslinking of the biopolymer matrix compared to the sample without a modifier, which has lower optical densities and larger peak areas at the same wave numbers. The detected absorption bands with shifted wave numbers in the lower frequency range for the sodium sulfate-modified biocomposites indicate the influence of the modifier on the activation of the processes of chemical bonding of the biopolymer matrix, which improves the structuring of biocomposite material.

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