UDC 678.549 DOI 10.36910/775.24153966.2024.79.2

О.Л. Садова, М.І. Вишинський

Луцький національний технічний університет

ДОСЛІДЖЕННЯ МЕХАНІЧНИХ ВЛАСТИВОСТЕЙ ТА СТРУКТУРИ БІОКОМПОЗИТІВ, НАПОВНЕНИХ ПОДРІБНЕНИМИ СТЕБЛАМИ ЗЕРНОВИХ КУЛЬТУР

В статті досліджено міцність на стискання біокомпозитних матеріалів на основі глютинової матриці, яку готували за різного співвідношення компонентів. Як напонювач для біокомпозитних матеріалів використано подрібнені стебла зернових культур. Досліджено міцність на стискання біокомпозитів залежно від ступеня підсушування композиції. Проведення додаткової термічної обробки забезпечило підвищення механічних характеристик біококомпозитів. Ударну в'язкість матеріалу визначено залежно від вмісту наповнювача, ступеня підсушування та тиску пресування композиції, а також проведення додаткової термічної обробки біокомпозитів. Структуру біокомпозитів досліджено методом ІЧ-спектроскопії на основі аналізу функціональних груп.

Ключові слова: *розчин глютину, подрібнені стебла зернових культур, міцність на стискання, ударна в'язкість, ступінь підсушування, ІЧ спектроскопія.*

O. Sadova, M. Vyshynskyi

STUDY OF MECHANICAL PROPERTIES AND STRUCTURE OF BIOMPOSITS FILLED WITH CHOPPED STALKS OF CEREALS CROPS

The article examines the compressive strength of biocomposite materials based on a glutinous matrix, which was prepared with different ratios of components. Chopped stalks of grain crops are used as a filler for biocomposite materials. The compressive strength of biocomposites was studied depending on the degree of drying of the composition. Additional heat treatment of biocomposites was carried out in order to increase the mechanical properties of biocomposites. The impact strength of biocomposites is determined depending on the content of the filler, the degree of drying of the composition, the pressing pressure of the composition and the additional heat treatment of biocomposites. Analysis of the structure with the detection of functional groups of biocomposites was investigated by IR spectroscopy.

Key words*: glutin solution, chopped stalks of cereal crops, compressive strength, impact strength, degree of drying IR spectroscopy.*

Formulation of the problem. In modern industry, synthetic discrete fibers are mainly used to reinforce composite materials. However, recently, the development of green materials and technologies encourages scientists and industry to use natural fibers and matrices for the formation of composite materials [1]. The use of fibers of natural origin as a filler in a thermoplastic matrix is an alternative for the production of inexpensive and ecological composites using them as a commodity plastic or packaging material [2]. Currently, many different natural fibers of plant origin have been investigated. Their unique properties have been revealed. The use of natural fibers for reinforcing plastics allows to improve their mechanical properties, in particular strength. Composite materials have been developed based on synthetic thermoplastic matrices [1] containing hemp, jute straw, paper mulberry, empty oil palm fruits, wood, wheat, barley, kenaf, rye, rice husk, bamboo, flax, reed, oats, sisal, grass, coconut coir, ramie, pineapple leaf fiber, banana fiber and papyrus. However, there is a need to develop and conduct research on biocomposite materials based on matrices of natural origin, which ensures a high degree of biodegradability and simplifies the disposal of biocomposite products at the final stage of the life cycle.

Analysis of recent studies and publications. Fibers add to composite materials in order to increase the thermal stability of the matrix, which ensures the ability to operate biocomposite products at higher temperatures. It has been proven that the addition of long fibers reduces the kinetics of water absorption and the formation of biocomposites with a low moisture content. It was revealed by the IR-spectroscopy method that the addition of cellulose fibers leads to a change in the structure of the thermoplastic matrix. The absorption peaks corresponding to hydroxyl groups are shifted to lower wavenumbers. This indicates the existence of hydrogen interaction between the components. The prepared samples are completely biodegradable. The components formed during the decomposition are harmless if they get into the environment [2].

The authors of the work [3] developed highly filled composites based on starch, which are reinforced with natural fibers (flax, bagasse, banana, date palm). The composites were prepared by pressing under a pressure of 5 to 20 MPa and a temperature of 130 to 160°C. It was established that composites with a fiber content of 50-70% have the highest tensile strength and modulus of elasticity. It was established that the mechanical properties of the composites significantly deteriorated when the fiber content increased to 80% due to insufficient amount of starch binder.

The formation of biocomposites filled with flax, bagasse, banana and date palm fibers was carried out by pre-heating the composite and pressing under a pressure of 5 MPa at a temperature of 150 °C for 30 min. The bamboo-reinforced starch-based composite was prepared by pressing under a pressure of 20 MPa at a temperature of 130 °C for 5 min. The composite based on starch and hemp was prepared by pressing under a pressure of 10 MPa at a temperature of 130 °C for 5 min. All fibers, except bamboo and hemp, were treated with alkali (NaOH) before preparing the composite. Composite samples filled with fibers of flax, bagasse, date palm and banana in the amount of 50-60 wt. %, have the highest tensile strength. These strength values are 8-15 times higher than the strength value of the composite based on starch binder without fiber content (less than 4 MPa).

Composites of polymer and natural fiber absorb moisture in a humid environment. Moisture absorption affects the matrix-fiber interface, which leads to low stresses between the matrix and the fiber. The movement of water in the composite can be explained by the presence of defects in the matrix (voids, pores and cracks). Water absorbed by the matrix is of two types: free and bound. Free water is water molecules that move freely through the voids, and bound water is water molecules that are bound to the polar groups of the matrix [3].

According to the literature, the moisture absorption of starch/natural fiber composites is highly dependent on the type of fiber and its content. It was established that each type of fiber has a different cellulose content, and fibers with a high cellulose content significantly reduce the moisture absorption of the resulting composite. Mehanny and etc. investigated the influence of thermoplastic starch (TPS) matrix with different content (0, 20, 40, 60 and 80%) of bagasse fibers treated in NaOH on the moisture absorption of the obtained composite. The moisture absorption of the composite with a starch-based matrix without fibers was more than 53%, while at the lowest fiber content of 20% it was 48%. Moisture absorption decreases to 36% with an increase in fiber content to 80% [4]. According to Elsayed et al. [5, 6] increasing the content of NaOH-treated flax fiber from 0 to 60% led to a decrease in the moisture absorption of the TPS/flax composite from 48% to 38%.

It was established by the TGA method that the thermal decomposition of thermoplastic starch occurs in three main stages. The first stage - the formation of a peak on the crooked line at a temperature of 100°C is explained by the evaporation of water. The second stage – the formation of a peak on the crooked line near 200°C is associated with the evaporation of glycerol. The third stage – the formation of a peak around 330°C on the crooked line is associated with the thermal decomposition of starch. Composites with a high content of natural fibers based on a starch binder are a promising material for the production of panels for housing, automobiles and decorative applications [7].

The study of thermoplastic composites based on wheat gluten (the content varied from 0 to 20 wt.%), which were formed by pressing, is presented in the article [8]. The maximum tensile strength of thermoplastic starch/wheat gluten composites (1.1 MPa) was obtained using 10 wt.% wheat gluten. Crosslinking between protein chains of wheat gluten caused an increase in the tensile strength of thermoplastic starch/wheat gluten system composites. The temperature during maximum loss mass (TGA) of thermoplastic starch/wheat gluten composites was higher than that of thermoplastic starch. In addition, wheat gluten reduces water absorption.

Setting tasks. The purpose of the work is to study the mechanical properties and structure of biocomposite materials, based on a glutin solution of different concentrations.

Presentation of the main material. In order to increase the compressive strength of biocomposites, it is necessary to establish the optimal ratio of the components used to the formation of the biopolymer matrix. The content of chopped stalks of grain crops in biocomposite materials was 140 wt. parts with fraction of 0.7 mm. The degree of drying of the composition was 20% and 25%. The main heat treatment was carried out at a temperature of 150 °C with exposure for 2 hours. Additional heat treatment (TO2) was carried out at a temperature of 50 °C with exposure for 4 hours. The concentration of the glutin solution was 38%, 43% and 50%.

The strength of biocomposite materials (with the degree of drying of composition of 20%) without additional heat treatment (TO2) (Fig. 1) is 43.9 MPa and 57.0 MPa in the case of using a glutin solution concentration of 38% and 43%, respectively. The 23% higher compressive strength of biocomposites, the matrix of which was formed with a glutin solution concentration of 43%, can be explained by the presence of a smaller amount of unbound water in the materials. Unbound water prevents the formation of the maximum possible number of physical and chemical bonds between the components of the biocomposite system. During additional maintenance (exposure for 4 h at a temperature of 50 °C), the compressive strength of biocomposites, the matrices of which were formed with a glutin solution concentration of 38%

and 43%, increases by 19-22% and is 54.1 MPa and 73.2 MPa, respectively. This indicates additional structuring of biocomposites due to the removal of excess moisture from the biocomposite material during additional heat treatment.

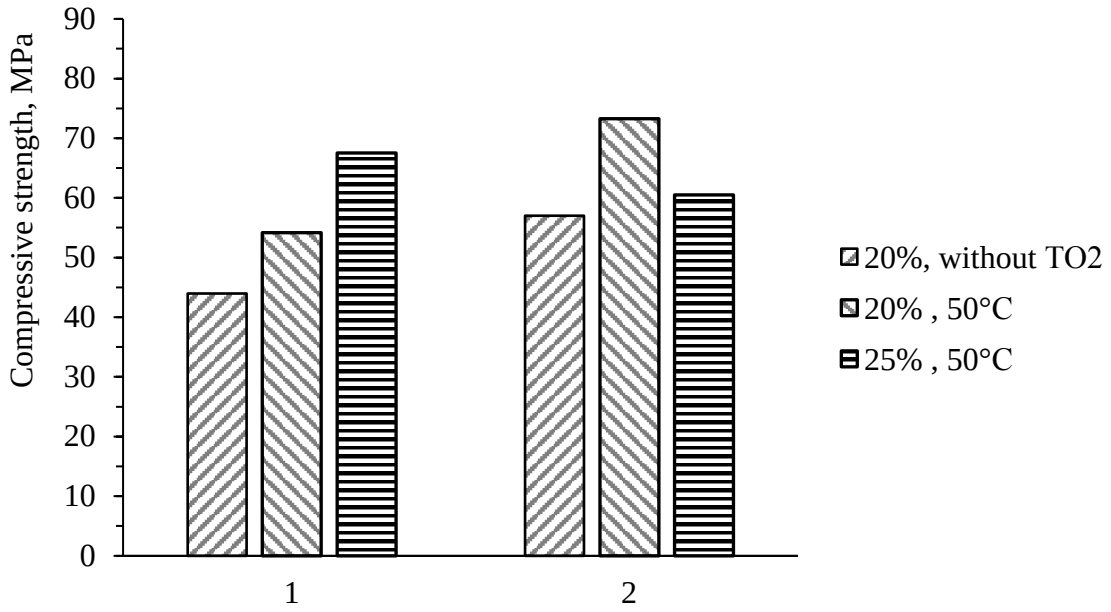


Fig. 1. **Compressive strength of biocomposites under different modes of glutin matrix formation:** 1 **– concentration of glutin solution 38%; 2 – concentration of glutin solution 43%**

Compressive strength increases by 20% (67.5 MPa) with an increase in the degree of drying of the composition up to 25% for biocomposites, the matrix of which was formed at a concentration of glutin solution of 38%. The increase in the strength of biocomposites can be explained by a higher degree of drying of the composition (additional moisture removal), which provided a higher degree of structuring of the material. The compressive strength decreases by 23% in the case of an increase in the degree of drying of the composition for biocomposites, the matrix of which was formed with a concentration of glutin solution of 43%. In this case, the decrease in strength can be explained by the insufficient moisture content due to the use of less water for the formation of the biopolymer matrix, since the degree of drying of the composition was 25%. Therefore, optimal moisture content in the material is necessary to ensure a higher degree of structuring of biocomposites, as well as their strength.

Additional thermal treatment of TO2 was carried out (exposure for 4 h at a temperature of 50 °C) for composite samples with a concentration of 50% glutin solution. Additional thermal treatment of TO2 (exposure for 4 h at a temperature of 50 °C) was carried out for composite samples with a concentration of glutin solution of 50%. The degree of drying of the composition was 20% and 25%. Biocomposites filled with 150 wt. parts of chopped cereal stalks and a degree of drying of the composition of 20% have the highest compressive strength of 82.8 MPa (Fig. 2). The average mass loss of the biocomposite sample after additional heat treatment is 0.06 g (Table 1).

The compressive strength of biocomposites decreases by 63% with an increase in the degree of compression of the composition to 25%, which is 50.9 MPa. The average mass loss of the biocomposite sample after additional heat treatment is 0.08 g. The decrease in compressive strength can be explained by the excessive removal of moisture (mass loss of 25%) from the volume of the material with a high content of filler, which did not allow the formation of the maximum possible number of bonds in the material.

For this biocomposite, absorption bands were detected on the IR spectrogram (Fig. 3) at frequencies of 1458.25 cm^{-1} with optical density D=0.442 and half-width b=7.72 cm^{-1}, 1655.00 cm^{-1} with optical density D =0.477 and half-width b=11.58 cm^{-1}, 1701.29 cm^{-1} with optical density D=0.447 and half-width b=9.65 cm^{-1}. The obtained absorption bands indicate the presence of deformation vibrations of O-H-, C-H, N-H groups and valence vibrations of double bonds -C=C, -C=O, -N=O and -C=N, the number of which increases during heat treatment. In the areas of higher wave numbers, absorption bands were recorded at frequencies of 2345.54 cm-1 with optical density D=0.486 and half-width b=32.80 cm^{-1} and 2364.83 cm^{-1} with optical density D=0.503 and half-width b=21.22 cm^{-1}.

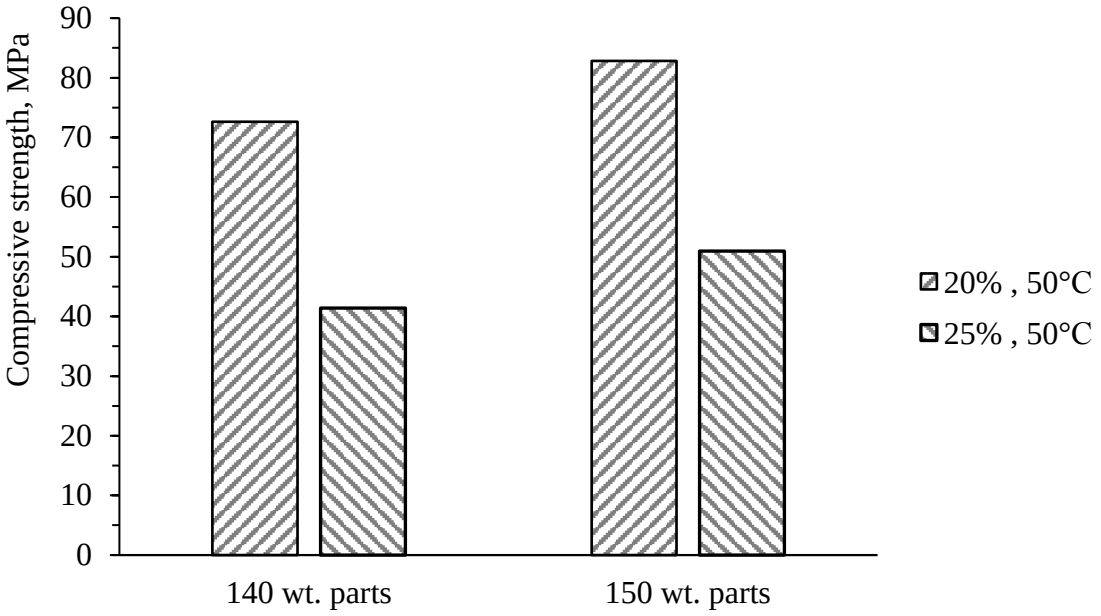


Fig. 2. **Compressive strength of biocomposites with a concentration of glutin solution of 50%**

Table 1.

Mass loss of biocomposite samples during preliminary heat treatment (drying)

The content of chopped stalks of grain crops, wt. parts	The degree of drying of the composition					
	20%			25%		
	m_0, g	m_1, g	Δm, g	m_0, g	m_1, g	Δm, g
140	8,74	8,56	0,18	8,02	8,08	-0,06
150	8,79	8,71	0,08	8,14	8,22	-0,08

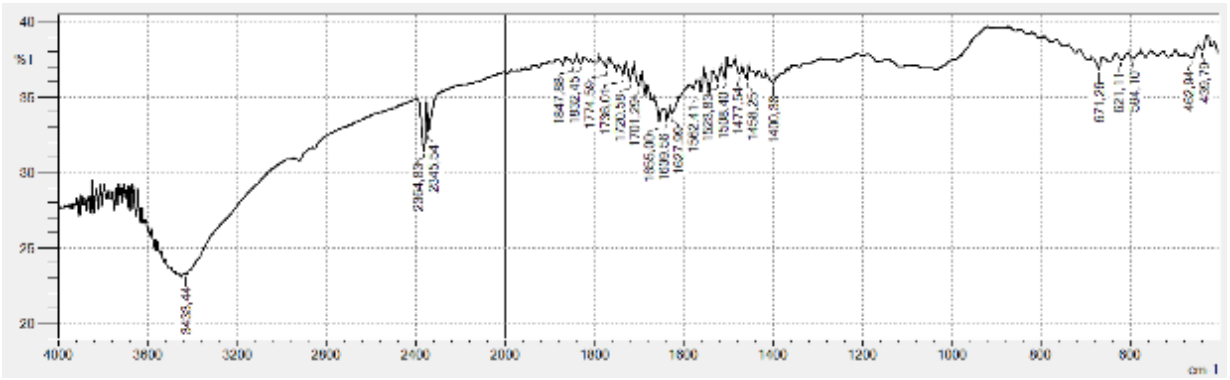


Fig. 3. **IR spectrogram of a biocomposite based on a glutin matrix with a concentration of 50% glutin solution, which contains 150 wt. parts of chopped stalks of grain crops with a degree of drying of 20% (Fig. 2)**

The compressive strength of biocomposites filled with 140 wt. parts chopped stalks of grain cropsand the degree of drying of the composition 20 % is 72.6 MPa. This value of strength is lower by 12% compared to the samples that have the maximum value of compressive strength (82.8 MPa) for the given ratio of components of the polymer matrix. The average change in the mass of the sample after additional heat treatment is +0.18 g. The lower compressive strength of these samples can be explained by the lower content of the filler, which performs a reinforcing function.

Among the studied samples (Fig. 2) the lowest (2 times compared to the maximum value) compressive strength (41.4 MPa) was obtained for biocomposites containing 140 wt. parts of the filler, with a degree of drying of the composition of 25%. The average change in the mass of the sample after additional heat treatment is +0.08 g. The low compressive strength of this biocomposite can be explained by the low content of the filler (140 wt. parts) and the degree of drying of the composition (20%), which is associated with a decrease in the structuring of the material due to excess moisture content. Moisture, which is in a

vapor state, does not have time to be removed during heat treatment. Moisture condenses in the pores and voids of the material, which prevents its structuring.

Biocomposite samples were formed to study the impact toughness. The optimal composition and technology for these biocomposites were selected based on the results of compressive strength studies. Biocomposite samples were formed by pressing the composition in a mold under different pressures (8 MPa or 11 MPa). The duration of the main heat treatment of the samples was 2 hours at a temperature of 150 °C.

Biocomposites (sample No. 3, Table 2) containing 140 wt. parts of chopped stalks of grain crops with a degree of drying of the composition of 25%, formed under a pressure of 11 MPa. These biocomposite samples were subjected to additional heat treatment at a temperature of 50 °C with exposure for 4 hours. The obtained higher values of the impact toughness of biocomposites are ensured by a high degree of drying of the composition at the forming stage, which allows the removal of excess moisture. Higher pressing pressure of the composition and additional heat treatment of biocomposites at a low temperature also contribute to the formation of a greater number of physical and chemical bonds between the components of the biocomposite material.

Table 2.

Composition and of forming technology of biocomposites for the study of impact toughness

Sample No	Filler content, wt. parts	Degree of drying, %	TO2, 50 °C 4 hours	Pressing pressure, MPa	KC, kJ/m^2
1	140	20	+	8	4,82
2	140	25	-	8	2,82
3	140	25	+	11	6,56
4	150	20	+	8	4,25
5	150	25	+	8	3,05
6	150	20	-	8	3,92
7	150	20	-	11	1,52

Biocomposite samples No. 1, formed at a lower degree of composition drying (20%) and lower pressing pressure (8 MPa), have 27% lower values of impact toughness (4.82 kJ/m^2) compared to biocomposites No. 3. This indicates the removal of an insufficient amount of moisture from the volume of biocomposite material for this filling (140 wt. parts) of the composition. Moisture forms microcracks by evaporating during additional heat treatment.

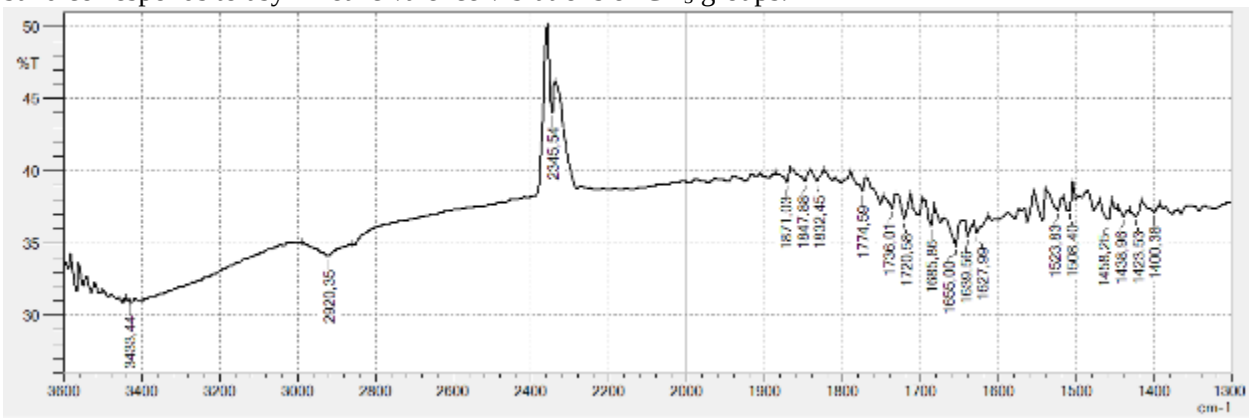
Among the biocomposites with a content of 140 wt. parts of chopped stalks of grain crops, the lowest impact toughness (2.82 kJ/m^2) has the samples formed according to technology No. 2 (degree of drying 25%, pressing pressure 8 MPa). The low values of the studied characteristic can be explained by residual moisture in the material, since no additional heat treatment was performed for these biocomposites.

Among the biocomposite materials with a content of 150 wt. parts of chopped stalks of grain crops, the highest impact toughness (4.25 kJ/m^2) have biocomposite samples formed by technology No. 4. However, this value is 35% lower compared to the value of impact toughness of biocomposite formed by technology No. 3. The 28% lower value of impact toughness (3.05 kJ/m^2) of biocomposites formed according to technology No. 5 can be explained by the formation of an insufficient number of bonds between the components of the composite system due to the high degree of filling (150 wt. parts) and the degree of drying (25%) of the composition due to insufficient wetting of the filler with the glutin matrix.

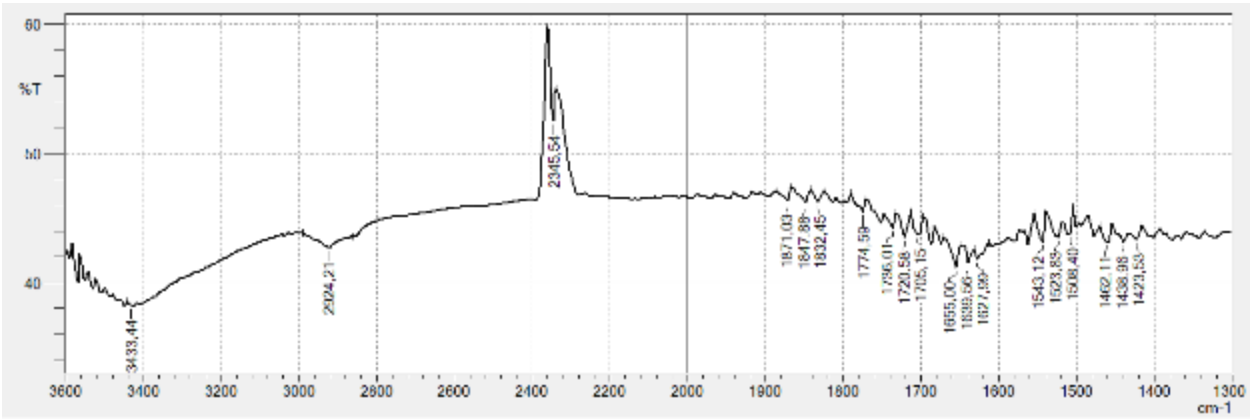
To study the impact toughness, biocomposites were formed with the content of the filler and the degree of drying of the composition, such as biocomposite No. 4 without additional heat treatment (No. 6 and No. 7). Impact toughness (3.92 kJ/m^2) is 8% lower compared to biocomposite No. 4 in biocomposites formed by technology No. 6. The lowest impact toughness is 1.52 kJ/m^2 (2.8 times compared to No. 4 and 4.3 times compared to No. 3) have biocomposites formed according to technology No. 7. The obtained low impact toughness of biocomposites, the degree of drying of the compositions of which is lower (20%), indicate the presence of excess moisture in the volume of the material, which prevents structuring. Carrying out additional heat treatment at a low temperature allows to increase the degree of structuring of biocomposites due to the formation of more bonds due to the removal of excess moisture.

A complex spectrum of transmission bands in the frequency range of 1400 cm^{-1}... 1900 cm^{-1} was revealed for the developed biocomposites. The most characteristic transmission bands (Fig. 4, a) at frequencies of 1438.96 cm^{-1} with optical density D=0.434 and half-width b=7.72 cm^{-1}, 1655.00 cm^{-1} with optical density D=0.459 and half-width b=13.51 cm^{-1}, 1720.58 cm^{-1} with optical density D=0.437 and half-width b=9.65 cm^{-1} was recorded for biocomposite material No. 1 (Table 2), which contains 140 wt. parts

of the filler with a degree of drying of the composition of 20% and a pressing pressure of 8 MPa. These bandwidths correspond to symmetric deformation vibrations of $–CH_3$-groups and valence vibrations of –C=O-groups. The fixed transmission band at the frequency of 2345.54 cm^{-1} with optical density D=0.357 and half-width b=9.65 cm^{-1} corresponds to valence vibrations –P–H. The transmission band at the frequency of 2920.35 cm^{-1} (optical density D=0.467 and half-width b=63.65 cm^{-1}) was detected. This transmission band corresponds to asymmetric valence vibrations of CH_3 groups.



a



b

Fig. 4. **IR spectrograms of biocomposites No. 1 (a) and No. 4 (b) (Table 2)**

Biocomposite material No. 4 (Table 2), which contains 150 wt. parts of the filler with a degree of drying of the composition of 20% and a pressing pressure of 8 MPa is also characterized by transmission bands at similar frequencies (Fig. 4, b): 1438.96 cm^{-1} with an optical density D=0.365 and a half-width b=11.58 cm^{-1}, 1655.00 cm^{-1} with optical density D=0.385 and half-width b=11.58 cm^{-1}, 1720.58 cm^{-1} with optical density D=0.362 and half-width b=9.65 cm^{-1}. The transmission band has a larger half-width value of b=11.57 cm^{-1} at frequencies of 2345.54 cm^{-1} (optical density D=0.280).

The transmission band, which corresponds to the vibrations of the methylene group, is shifted to the region of higher frequencies up to 2924.21 cm^{-1} with optical density D=0.370 and half-width b=63.65 cm^{-1}. This indicates the activation of physicochemical processes of bond formation in the biocomposite. This material has lower values of optical densities compared to biocomposite material No. 1, which indicates a lower degree of structuring of the biocomposite system.

Conclusions. It was established that with a lower content of chopped stalks of grain crops (140 wt. parts) it is necessary to dry the composition until the moisture loss of 25% by weight. With a higher content of the filler (150 wt. parts), it is sufficient to dry the composition to a moisture loss of 20% by weight. This is economically beneficial, as the duration of the technological process is shortened, which will lead to a decrease in energy costs. Biocomposites filled with 150 wt. parts of chopped stalks of cereal crops and the degree of drying of the composition of 20% with a concentration of glutin solution of 50% have the highest compressive strength of 82.8 MPa. This material has a high degree of structuring, as evidenced by the IR spectrogram of the biocomposite. It was established that it is necessary to increase the degree of drying of the composition to 25% in the case of a lower concentration of glutin in the matrix and a higher content of water in the composition. The compressive strength of these biocomposites is 54.1 MPa. Degree of drying of the composition of 20% is sufficient for biocompositions with a higher concentration of glutin solution

(43% and 50%), which is associated with a lower water content in the matrix. The strength of these biocomposites is higher (73.2 MPa). A higher concentration of glutin solution of 50% increases its viscosity. The IR spectroscopy method confirmed that biocomposite materials that contain less chopped stalks of grain crops (140 wt. parts) have a higher degree of structuring compared to biocomposites with a content of 150 wt. parts of filler.

References

1. MD Recycled Plastic Biocomposites. Rezaur Rahman, Muhammad Khusairy Bin Bakri., 1st Edition - January 24, 2022.
2. Ahmad F., Choi H.S., Park M.K. Natural fiber composites selection in view of mechanical, light weight and economic properties. Macromolecular materials and engineering. 2015; 10-24.
3. Grigore M.E. Methods of recycling, properties and applications of recycled thermoplastic polymers. Recycling. 2017; 2(4).
4. Vazquez-Nunez E, Avecilla-Ramirez A, Rocio Lopez-Cuellar M. Green composites and their contribution toward sustainability. Polymers and Polymer Composites. 2021, Vol. 29(9S): 588-608.
5. Farah S, Anderson DG, Langer R. Physical and mechanical properties of PLA, and their functions in widespread applications—a comprehensive review. Adv Drug Deliver Rev 2016; 107(1): 367-392.
6. Siakeng R, Jawaid M, Ariffin H, et al. Mechanical, dynamic, and thermomechanical properties of coir/pineapple leaf fiber reinforced polylactic acid hybrid biocomposites. Polym Compos 2019; 40(5): 2000-2011.
7. Mishra R, Behera B, Militky J. Recycling of textile waste into green composites: Performance characterization. Volume 35, Issue10, October 2014: 1960-1967.
8. Thakur V, Singha A and Thakur M. Green composites from natural fibers: mechanical and chemical aging properties. Int J Polym Anal Charact 2012; 17: 401-407.