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МОДИФІКАЦІЯ ГЛЮТИНОВИХ БІОКОМПОЗИТНИХ МАТЕРІАЛІВ ГІДРОФОБНИМИ ДОБАВКАМИ

Проведено дослідження впливу гідрофобних добавок на межу міцності при стисненні біокомпозитних матеріалів, які мають глютинову матрицю та наповнені частинками деревного борошна. Введення гідрофобних добавок (оліфа Оксоль, соняшникова олія) обумовлено високою гідрофільністю наповнювачів рослинного походження. В результаті введення оліфи Оксоль в оптимальній кількості зафіксовано підвищення міцності при стисненні на 12-15 % порівняно з немодифікованими біокомпозитними матеріалами. Визначено характер руйнування модифікованих оліфою Оксоль біокомпозитних матеріалів під впливом стискаючого навантаження. Проведено порівняльну оцінку міцності біокомпозитних матеріалів з різним вмістом гідрофобних добавок.

Ключові слова: *біополімерні композити; наповнювач; пресування; міцність; напруження; хімічні зв'язки; адгезія; структура; пористість; механічні характеристики.*

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MODIFICATION OF GLUTIN BASED BIOCOMPOSITE MATERIALS WITH HYDROPHOBIC ADDITIVES

The influence of hydrophobic additives on the compressive strength of biocomposite materials based on a glutinous matrix and are filled with wood flour particles, was studied. The use of hydrophobic additives (drying oil Oksol, sunflower oil) is due to the high hydrophilicity of fillers of plant origin. As a result of the use of drying oil Oksol in the optimal amount, an increase in compressive strength by 12-15% was recorded compared to unmodified biocomposite materials. The nature of destruction of biocomposite materials modified with drying oil Oksol under the influence of compressive load was determined. A comparative assessment of the strength of biocomposite materials with different contents of hydrophobic additives was carried out.

Key words*: biopolymer composites; filler; pressing; strength; tension; chemical bonds; adhesion; structure; porosity; mechanical characteristics.*

Formulation of the problem. Biocomposite materials have many advantages compared to polymer composite materials containing synthetic components. This concerns environmental friendliness, reproducibility of raw materials, low density and low manufacturing cost. Taking into account the advantages of biocomposite materials, it is possible to note the high degree of efficiency and perspective of using such materials in various branches of industry for the manufacture of furniture elements, sports equipment, interior parts of vehicle interiors, household products, containers and device housings. Biocomposite materials are safe at different stages of the production process and are not harmful to the environment after destruction of the product. A high ability to recover raw materials ensures production stability and economic development. Components for the formation of biocomposites can be materials obtained by processing waste from the woodworking, agricultural, and food industries. Components of natural origin provide high mechanical characteristics of biocomposite materials, but due to their high hydrophilicity, they are able to intensively absorb moisture. The decrease in mechanical characteristics occurs due to the destruction of the physical and chemical bonds between the structural elements of the components of the biocomposite material. Otherwise, favorable conditions are created for the development of microorganisms (bacteria, fungi), which lead to biodegradation with the formation of new substances. There is a problem of providing effective hydrophobic protection or increasing moisture resistance of biocomposite materials that contain vegetable fillers. In this case, biocomposite materials require the use of modifying additives, which are characterized by high hydrophobicity. At the same time, it is necessary to determine the ability of fillers to provide high adhesive strength to the polymer matrix and to form biocomposite products with high mechanical characteristics after the introduction of modifying substances.

Analysis of recent research and publications. Composite materials, which are obtained from natural sources, have attracted considerable interest in recent years due to the desire to increase the environmental friendliness of production. This situation is beneficial for global communities to reduce dependence on synthetic materials [1]. It is possible to use a wide range of materials of natural origin as fillers of biocomposites. Fillers can significantly improve the mechanical characteristics of biocomposite materials [2, 3].

The high rate of degradation of natural components ensures intensive destruction of biocomposite products after the end of their operation. Such products are in landfills or are under the influence of atmospheric factors in the natural environment. However, this process is not permissible if the biocomposite

product is being operated, stored or transported. Determining the ability of a material to biodegrade is considered taking into account many factors (chemical composition of the material, humidity, temperature change), which requires the presence of special recommendations that determine the influence of such parameters. In the process of developing biocomposite materials using natural fibers, moisture absorption is a critically important factor that can significantly affect the mechanical properties of the biocomposite. The importance of the factor increases if the matrix is a bio-based polymer, as these materials absorb more moisture than their synthetic-based counterparts. It has been proven that biocomposites are not suitable for use in water, so this point must be taken into account during the operation of the products [4].

The absorption of moisture in biocomposites is caused by the natural hydrophilicity of plant fibers [5]. Moisture absorption in biocomposites is due to the natural hydrophilicity of plant fibers. The volume and content of fibers and the ambient temperature significantly affect water absorption. At the same time, there is an increase in the effect in biocomposites with a higher fiber content and environmental temperature [6].

The use of hydrophobic additives makes it possible to increase the water resistance of biocomposite products, but in most cases, there is a decrease in mechanical characteristics. A modifying additive (paraffin) improves manufacturability during compression of the composition, which contains finely dispersed particles of wood flour. As a result of the use of paraffin, the density of the biocomposite material increases, which improves the material's resistance to static loads [7].

In the case of introducing citric acid and glutaraldehyde into the polyvinyl alcohol, which contains banana pseudostem fibers, water resistance is increased due to the presence of hydroxyl groups. Biocomposite material with pseudostem fibers treated with alkali, banana has a maximum tensile strength of 34.2 MPa and water absorption of only 60% [8].

Chemical treatment changes not only the surface layer of the fibers, which affects the nature of the interaction between the fiber and the matrix, but also changes the structure and density of elementary fibers [9]. The addition of Posidonia oceanica leaves (POL) improved the mechanical properties of PLA-based polymer matrices and accelerated their decomposition [10]. The paper [11] investigated the properties of Sugar Palm Fiber (SPF), which are used for the development of fishing boats. These fibers have sufficient resistance to water permeability and high mechanical strength. Although lignocellulosic fibers (SPF) have advantages over other natural fibers, they have a tendency to absorb water over time [12]. This reduces their wettability by the hydrophobic polymer resin, which leads to the absence of interfacial bonding between the fiber and the matrix. This condition limits the adhesive strength of biocomposites and leads to a decrease in mechanical properties [13]. In this case, the authors of the paper recommend pre-treatment of SPF using physical or chemical methods [14, 15]. The processed lignocellulosic fiber has a rougher surface, which helps to increase the number of activation zones for the formation of a chemical bond with the matrix. The creation of a strong adhesive bond at the fiber-matrix interface ensures high cohesive strength of the biocomposite and ensures the use of lignocellulosic fiber for the manufacture of household products, car structures, and also in the aerospace industry. The main benefit of SPF is the durability of the fiber due to less exposure to heat and moisture compared to coir or other natural fibers. SPF is resistant to the influence of salt water, so the fiber can be used for the operation of biocomposite products in a seawater environment.

Setting tasks. The purpose of the work is to determine the cohesive strength of glutinous biocomposite materials, which are filled with finely dispersed wood flour and modified with hydrophobic additives (dry oil Oksol, sunflower oil).

Presentation of the main material. The homogeneity of the composition is ensured by mixing the components with a rotation frequency of the working body of 300 Hz. Pressing of the composition is carried out in a press mold using a hydraulic press with a speed of movement of the lower traverse of 25 mm/s. Heat treatment consisted in heating the mold with the composition to a temperature of 150°C for 90 minutes, followed by cooling and removal of the biocomposite sample. Compressive strength was determined according to the ASTM D695 "Compression Testing of Rigid Plastics" method.

The compressive strength limit of biocomposite materials with an optimal content of wood flour, which do not contain additives, is 46.2 MPa (Fig. 1). The use of a modifying additive in the amount of 2-4 parts by weight leads to an increase in the compressive strength limit by 5%, which is associated with the arrangement of filler particles due to the introduction of the additive. The modifying additive performs a lubricating function, which reduces the coefficient of friction and reduces the resistance to the movement of wood flour particles during the pressing operation. Therefore, an ordered homogeneous structure is formed. A further increase in the drying oil content leads to a decrease in compressive strength to 28.7 MPa, which is 37-42% less compared to the strength values of biocomposites without the content of

modifying substances. This is due to the increased content of the modifying additive, which performs the function of a plasticizer. Molecules of drying oil dissolve in the glutinous matrix, which leads to a decrease in the number of physical bonds between macromolecules of amino acids of the biopolymer matrix.

Conducting preliminary heat treatment of the composition, which ensured moisture loss in the amount of 10% by mass, leads to a sharp increase in the compressive strength limit of biocomposite materials to 100.3 MPa. This treatment made it possible to increase the mechanical characteristics of biocomposites by 50-55%, since the removal of excess water ensures the formation of additional physical bonds between the glutinous matrix and the filler.

The introduction of 2-4 parts by weight of drying oil per 100 parts by weight of the binder leads to a 12-15% increase in the compressive strength of biocomposites compared to the strength of the biocomposite material without a modifying additive. The use of a hydrophobic additive ensures a reduction in the porosity of the biocomposite material, since the drying oil additionally performs the function of a lubricating additive. In the case of formation of biocomposites with a smaller amount of moisture, amino acid macromolecules approach, as water molecules dissolve the biopolymer matrix. Water is an inhibitor of the structuring process of biopolymer material.

Strength limit of biocomposites containing up to 10 part by weight of the modifying additive decreases by 35-38% compared to the strength of biocomposites, which have an optimal drying oil content in the amount of 2-4 parts by weight. This is explained by the excess content of drying oil, the concentration of which increases when water is removed from the composition during preliminary heat treatment. Molecules of drying oil prevent the formation of physical bonds between the hydroxyl groups on the surface of the organic filler and the active groups of the glutinous binder.

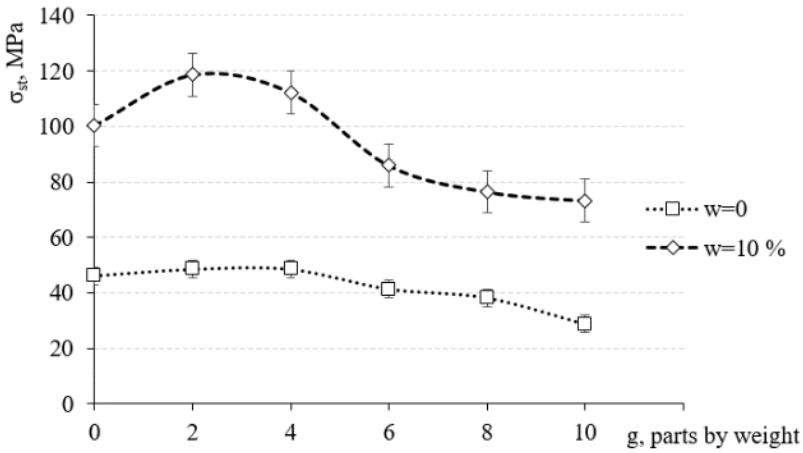

Fig. 1. **The dependence of the compressive strength of biocomposites on the content of drying oil Oksol in the composition and the degree of moisture loss of the composition**

Destruction of biocomposite samples, the compositions of which contain moisture and 2 parts by weight drying oil Oksol, occurs through the formation of a crack, which is located at an angle of 45 ° to the direction of action of the destructive load (Fig. 2, a). This indicates the resistance of the biocomposite material to mechanical stress, as the material perceives elastic deformation and breaks brittlely without plastic deformation. In the case of compression of biocomposite samples with the content of 10 parts by weight drying oil Oksol there is a displacement of material layers with the formation of delaminations (Fig. 2, b). This is due to the presence of a modifying additive that forms individual inclusions. They are a stress concentrator, as a heterogeneous structure is formed due to the low solubility of oil in the biopolymer matrix in the presence of moisture.

The destruction of biocomposite samples, the compositions of which have a 10% smaller amount of moisture, occurs similarly to the nature of the destruction of biocomposite samples, the compositions of which did not lose moisture (Fig. 3). Crack propagation in a biocomposite sample containing 2 parts by weight of drying oil Oksol occurs at an angle of 45° to the direction of the load (Fig. 3, a).

This indicates the absence of plastic deformation, which is associated with the formation of a dense structure without defects and concentrators.

Under the influence of a static compressive load, biocomposite samples with a content of a modifying additive of 10 parts by weight destroy with the formation of a crack, which is also located at an angle of 45° (Fig. 3, b).

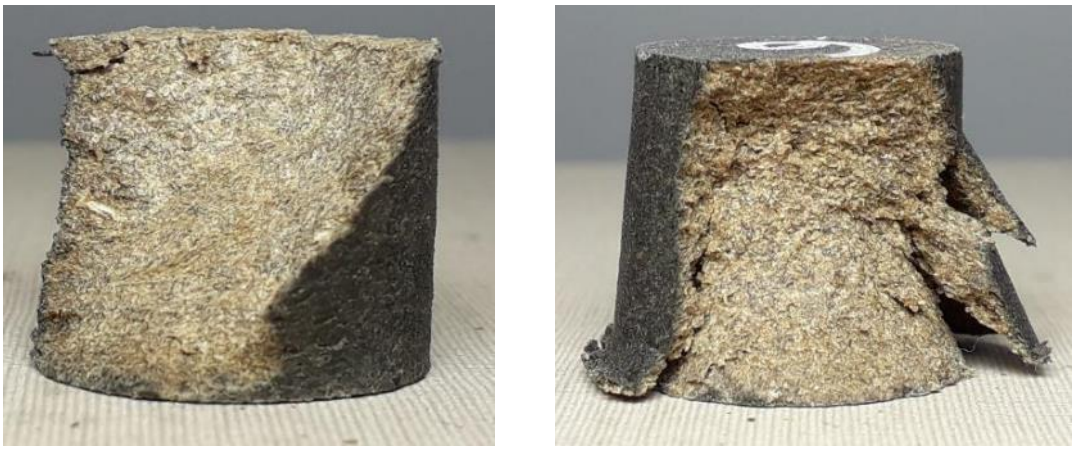

Fig. 2. **The general appearance of biocomposite samples (without removing moisture from the composition) after destruction with content of drying oil Oksol: a – 2 parts by weight.; b – 10 parts by weight**

This indicates the ability of the biocomposite material to resist plastic deformation, since after heat treatment, the molecules of oils in the glutinous matrix dissolve in the absence of moisture. In biocomposites, a homogeneous structure is formed, but the strength decreases due to an insufficient number of physical and chemical bonds.

Fig. 3. **The general appearance of biocomposite samples (with removal of 10% of moisture from the composition) after destruction with content of drying oil Oksol : a – 2 parts by weight.; b – 10 parts by weight**

An increase in the strength limit under compression from 47.8 MPa to 49.4 MPa (Fig. 4) occurs in the case of the introduction of sunflower oil in the amount of 2 parts by weight. This is due to the small content of the lubricant additive, which has a dominant effect on the process of compacting the composition. The compressive strength limit decreases by 22-26% with an increase in the content of the additive to 4-10 parts by weight, which is due to the plasticizing effect of the modifying additive.

Preliminary treatment of the composition ensures removal of 10%. moisture This leads to a 33-35% decrease in the strength limit of biocomposites that contain sunflower oil in the amount of 2 parts by weight, compared to biocomposites without a modifying additive. The introduction of a larger amount of sunflower oil (4-10 parts by weight) leads to a further decrease of this characteristic by 13-15%, which is due to the increased content of the modifying additive.

The value of the strength limit of biocomposites, the compositions of which have a lower amount of moisture by 10%, is 58-67 MPa. The strength of biocomposites, the composition of which was not thermally treated to remove moisture, is 38-49 MPa. This indicates the ability of the biocomposite material to form a denser structure in the case of moisture removal from the composition, since during the main heat treatment

at a temperature of 150° C, water molecules are removed. This leads to the appearance of delaminations and cavities, which are stress concentrators and reduce the cohesive strength of the biocomposite material.

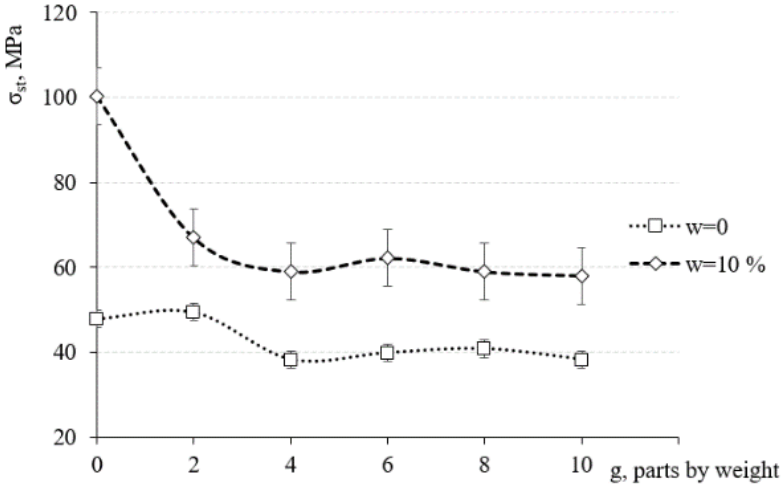

Fig. 4. **The dependence of the compressive strength of biocomposites on the content of sunflower oil in the composition and the degree of moisture loss of the composition**

Among biocomposites with a similar content of modifying additives, an increase in the compressive strength values of biocomposites whose compositions were thermally treated to remove moisture (10%) was found, from the range of values of 38-49 MPa to the range of values of 73-118 MPa. This is due to the ability of the oil to transition into a solid phase due to the removal of the volatile solvent during heat treatment, which causes the oil molecules to approach with the formation of bonds. Molecules of sunflower oil remain in the structure of the biocomposite material, since the modifying additive is not removed during heat treatment at a temperature of 150°C. The concentration of sunflower oil after heat treatment remains in the original state, which prevents the formation of the maximum number of physicochemical bonds between the active groups of macromolecules of the biopolymer binder and organic filler.

Conclusions and prospects for further research. Removing 10% of moisture from the composition during heat treatment provides a 50-55% increase in the compressive strength of biocomposite materials compared to biocomposites that contain excess moisture. This is due to the formation of the structure of the biopolymer matrix with higher cohesive strength in the case of the formation of the maximum number of physical bonds between glutin macromolecules.

Introduction of drying oil Oksol in the amount of 2-4 parts by weight to the composition leads to an increase in the strength limit of biocomposite materials by 12-15% compared to the unmodified material. Molecules of drying oil perform the function of a lubricating additive at the stage of pressing the composition so reduce the coefficient of friction between wood flour particles and ensures the formation of a dense structure of the biocomposite material due to the compact arrangement of particles in the glutinous matrix.

The destruction of biocomposite samples with a reduced amount of moisture in the composition and an optimal drying oil content (2-4 parts by weight) occurs as a result of the formation and propagation of a crack at an angle of 45° to the line of action of the compressive load. This type of destruction is explained by the absence of plastic deformation, since the formation of a rigid frame of the biopolymer matrix occurs due to the removal of the solvent from the drying oil during the heating of the composition in the mold. This additionally increases the cohesive strength of the glutinous matrix due to the formation of physical bonds between the components of the biocomposite material.

In the future, it is planned to determine the influence of the amount of compression force and the temperature of heating the composition on the mechanical characteristics of biocomposite materials that contain hydrophobic additives.

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