UDC 674.022:621.715 DOI 10.36910/775.24153966.2024.77.22

В.С. Мазурок, В.П. Кашицький

Луцький національний технічний університет

ОПТИМІЗАЦІЯ СКЛАДУ ТА ТЕХНОЛОГІЇ ФОРМУВАННЯ БІОКОМПОЗИТНОГО МАТЕРІАЛУ З ВМІСТОМ НАПОВНЮВАЧІВ РОСЛИННОГО ПОХОДЖЕННЯ

Визначено межу міцності біокомпозитних матеріалів, які наповнені частинками деревного борошна та подрібненими стеблами зернових культур в комплексному співвідношенні. Встановлено оптимальний склад наповнювачів природного походження, що дозволило отримати біокомпозитні матеріали з високою міцністю при стисненні. Визначено ефективність проведення попередньої термічної обробки композиції, що забезпечує видалення вологи в оптимальній кількості. Формування біокомпозитного матеріалу з високою щільністю досягається в результаті компактного розташуванням компонентів в біополімерній матриці. Досліджено вплив додаткової термічної обробки на міцність при стисненні, що визначає жорсткість глютинової матриці та еластичність подрібнених стебел зернових культур.

Ключові слова: *біополімерні композити; деревне борошно; подрібнені стебла; термічна обробка; пресування; міцність; пористість; хімічні зв'язки; адгезія; структура.*

V. Mazurok, V. Kashytskyi

OPTIMIZATION OF THE COMPOSITION AND FORMING TECHNOLOGY OF BIOCOMPOSITE MATERIAL WITH A CONTENT OF FILLERS OF PLANT ORIGIN

The compressive strength limit of biocomposite materials filled with wood flour particles and chopped stalks of grain crops in a complex ratio was determined. The optimal composition of fillers of natural origin has been established. This made it possible to obtain biocomposite materials with high compressive strength. The effectiveness of the preliminary heat treatment of the composition, which ensures the removal of moisture in the optimal amount, has been determined. The formation of a biocomposite material with high density is achieved as a result of the compact arrangement of components in the biopolymer matrix. The influence of additional heat treatment on compressive strength, which determines the stiffness of the glutinous matrix and the elasticity of the chopped stalks of cereal crops, was investigated.

Key words*:* *biopolymer composites; wood flour; chopped stalks; heat treatment; pressing; strength; porosity, chemical bonds; adhesion; structure.*

Formulation of the problem. The widespread use of a new class of polymer composite materials containing natural components is due to the high environmental friendliness of such materials and the developed raw material base. In the case of using natural binders and fillers, the harmful impact on the ecosystem is reduced sharply compared to synthetic components of polymer composite materials. This is due to the biocompatibility of the components, which do not impair environmental safety and do not pollute the environment during the manufacturing process of the products. In addition, under the influence of atmospheric factors, harmful substances are not formed during the destruction of biocomposite products. The raw material base for obtaining finely dispersed powders or fibers for the production of biocomposite products is replenished with a large amount of organic waste, which is generated as a result of the production of products in the textile, food, furniture and agricultural industries. Natural materials differ little in chemical composition, structure, and properties, so they do not require the development of a separate technological process for the preparation of fillers for mixing with the polymer matrix. This makes the process of waste processing easier and ensures the unification of the technological processes of preparing components for the formation of biocomposite products. However, it is necessary to take into account the morphological composition and physical and mechanical properties of natural fillers, which affects the technology and development of the technological process of forming biocomposite products. The structure of biocomposite materials is formed depending on the nature of the filler and the presence of active groups on its surface, as well as the ability to interact with the polymer matrix. This determines the physical and mechanical and operational properties of biocomposite products, the scope of which expands depending on the functional purpose.

The most common fillers are finely dispersed fillers, which are obtained as a result of processing all possible types of raw materials of plant origin. This makes it possible to make the technological process of forming products easier, but it is difficult to ensure an increase in the resistance of biocomposites to the influence of dynamic loads. This is achieved by using fibrous fillers, but at the same time, the technological process of product formation is complicated. Solving the problem is possible in the case of using fillers in the form of short fibers, which allows to simplify the technological process and obtain high values of mechanical characteristics. The relevance of the work is determined by the need to determine the optimal ratio between the content of fine particles and discrete fibers, which requires research into the processes of structuring and interphase interaction of components of natural origin.

Analysis of recent research and publications. In the forming process of biocomposite materials, a scheme of combining components is used [1, 2]. The components are polymer synthetic matrix and fillers of plant origin. This approach is beneficial for modern society to reduce dependence on synthetic materials [3]. Biocomposite materials differ from polymer composite materials by the type of filler, which is mainly plant fibers [4, 5]. Developments in the direction of creating biocomposite materials are primarily determined by environmental needs. A feature of biocomposite materials is the presence of components of natural origin. Under the influence of microorganisms and atmospheric factors, they disintegrate into separate components, which are completely safe [6]. The use of eco-safe components reduces harmful effects during the production of biocomposite products, which increases safety and occupational hygiene [7]. In this case, enterprises do not need to install complex and expensive ventilation systems and treatment facilities. In most cases, the use of natural fibers provides higher environmental friendliness compared to synthetic fibers (glass fiber, aramid fiber, carbon fiber) due to the reduction of carbon dioxide emissions and the consumption of less energy during production [8].

In addition, there are requirements for the economical use of materials based on non-renewable sources of raw materials due to limited oil and mineral substances. Their number in the earth's crust is constantly decreasing, as renewal takes place over thousands of years. Therefore, their use is not commensurate with the duration of recovery. Components of biocomposite materials can be obtained from food, wood processing, and agricultural waste [9]. On the one hand, waste materials are disposed of, and on the other hand, these industries are the main suppliers of renewable raw materials. This approach ensures the long-term existence of the raw material base, which is capable of recovery thanks to the cultivation of agricultural crops or energy plants.

The main advantages of biocomposites include availability and functional properties (eco-friendliness, high thermal insulation properties, good formability, low cost and the ability to restore the raw material base) [10]. In many cases, biocomposite-based materials provide weight reduction, increased stability of working parts of processing equipment, additional functional properties (damping and absorption of dynamic loads), as well as the ability to recycle [11]. In addition to the significant advantages of biocomposite products, there are a number of disadvantages that must be taken into account in order to obtain a quality product. First, the mechanical and operational properties of biocomposite materials are worse [12, 13] compared to polymer composite materials consisting of components of synthetic origin. However, with the use of modifying substances and chemical treatments, the properties of biocomposite materials can be significantly improved.

The intensive development of new polymers on a biological basis is associated with the high biodegradability of the matrix, which contains organic macromolecules. These biopolymers can be recycled in the process of technological transformations or synthesized using raw materials of biological resources [14]. A large group of biopolymers is represented by polysaccharides (cellulose, chitosan, starch, alginate, and pectin), consisting of tens or thousands of monosaccharides connected by glycosidic bonds. The group of synthesized thermoplastics includes biopolymers such as polylactic acid (PLA), polyhydroxyalkanoate (PHA), polyhydroxybutyrate (PHB), polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS), polycaprolactone (PCL) and thermosetting polymers obtained from vegetable oils and carbohydrates [15]. In some cases, mixtures containing both bio-derived and synthetic components are used. This ensures an optimal balance between productivity and positive environmental impact. Among the wide range of biopolymers, the most practical application is polylactic acid (PLA), which is obtained from corn starch and polyfurfuryl alcohol resin. Currently, there are many more types of biopolymers under development, including starch and vegetable oils. The work [16] determined the optimal pressing pressure of the composition (12 MPa), consisting of starch binder and wood flour particles. The use of a technological compression operation ensures the formation of a biocomposite material that has a high structure density due to the interaction of components with the formation of physical and chemical bonds.

Setting tasks. The purpose of the work is to determine the compressive strength limit of biocomposite materials based on gluten with a complex content of fillers (shredded cereal stalks and wood flour powder).

Presentation of the main material. The composition for the formation of biocomposite samples is a mixture of a glutinous binder and fillers of vegetable origin (chopped grains of cereal crops and wood flour) in a total amount of 100% (Table 1). The prepared composition was placed in a mold and compressed using a hydraulic press with a specific load of 120 MPa. Further, the mold with the composition was heated for 90 minutes at a temperature of 140°C. If necessary, additional heat treatment was performed. Additional heat treatment consisted in heating the biocomposite samples to a temperature of 50°C for 8 hours. The compressive strength limit was determined according to the ASTM D695 "Compression Testing of Rigid Plastics" method on cylindrical samples with a height of 30 mm and a diameter of 30 mm.

Table 1.

The ratio of filler content of multi-filled biocomposite material

№ sample	The content of chopped grains of cereal crops, %	Wood flour content, %
1	0	100
2	20	80
3	40	60
4	60	40
5	80	20
6	100	0

The limit of compressive strength of biocomposite materials containing wood flour (100%), the composition of which contains moisture, is 20.7 MPa (Fig. 1).

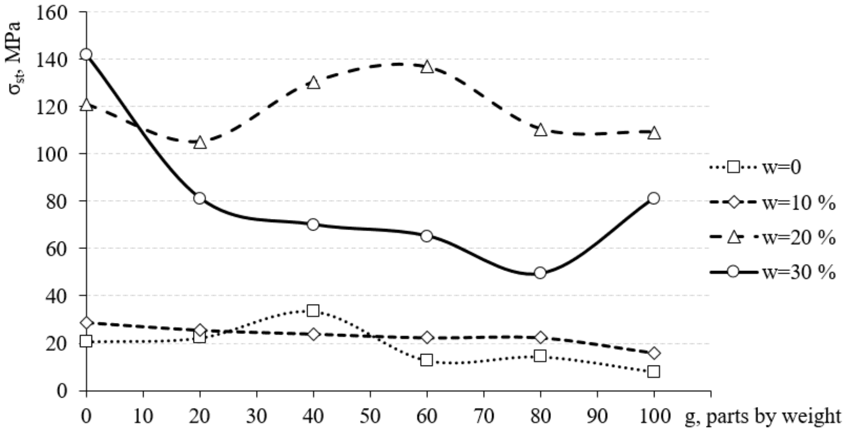

Fig. 1. **The influence of the content of chopped stalks of cereal crops on the compressive strength of biocomposite materials depending on the degree of moisture loss in the composition without additional heat treatment of the biocomposite**

With an increase in the content of chopped stalks of cereal crops, the content of wood flour decreases and, accordingly, is the difference between the maximum content of the filler in the mixture (100%) and the content of chopped stalks of cereal crops. The compressive strength increases by 38% in the case of using a mixture (40% chopped cereal stalks and 60% wood flour) compared to biocomposites without chopped stalks, because a biocomposite material with an optimal ratio of components is formed. The compressive strength limit decreases by 57-76% in the case of a further increase in the content of chopped stalks to 100% compared to the optimal content and reaches a minimum value of 8 MPa. This is due to the excessive content of chopped stalks in the biocomposite material, which form a heterogeneous structure due to the chaotic arrangement of particles in the biopolymer matrix.

The compressive strength of biocomposite materials increases by 27% in the case of preliminary heat treatment, which consists in removing moisture in the amount of 10% from the composition, compared to biocomposites without preliminary treatment of the composition. Such materials contain 100% wood flour and do not contain chopped cereal stalks. The increase in compressive strength is due to the formation of a biocomposite material that contains less moisture. This ensures the structuring of the biocomposite material with less porosity, as intensive moisture release occurs during heating of the composition in the mold. Accordingly, the formed cavities act as structural defects, which reduce strength under compression. A uniform decrease of 12-45% in compressive strength occurs with an increase in the content of chopped stalks, which is associated with an increase in the degree of chaos in the arrangement of chopped stalks.

Biocomposite materials, the compositions of which lost 20% of moisture as a result of preliminary heat treatment, have a significant increase in compressive strength by 82% compared to biocomposites without preliminary heat treatment of the composition. This increase is due to the removal of moisture from the composition, which contains 100% wood flour. It is much easier to remove moisture from the powder filler compared to the particles of the stalks of grain crops, which ensures the formation of a homogeneous structure. An increase in the strength limit under compression to the maximum values of 130.6 MPa and 136.9 MPa occurs in the case of the introduction of chopped stalks into the composition of biocomposites in the amount of 40-60%. This is explained by the presence of an optimal amount of moisture in the composition, which ensures the elasticity of the stalk particles without destruction during pressing of the composition. As a result, a dense structure is formed with a compact arrangement of wood flour particles and chopped stalks in the biopolymer matrix.

A sharp increase in the strength limit of biocomposite materials to 141.7 MPa occurs as a result of preliminary heat treatment of the composition, which ensures the removal of moisture in the amount of 30%. This provides an increase in compressive strength by 85% compared to biocomposite materials whose compositions contain the maximum amount of moisture (without additional heat treatment). An increase in the content of chopped stalks in the range of 20-60% in the biocomposite material leads to a 43-53% decrease in their compressive strength. Removing moisture from the composition complicates the process of compaction of the biocomposite material, as the stiffness of the stalks increases. Such stalks lose elasticity, which leads to their destruction during pressing of the composition. The lowest value (49.6 MPa) of the compressive strength limit of the biocomposite material is obtained with a content of chopped stalks of 80%. The formation of a composition consisting of 100% chopped stalks leads to an increase in the strength limit to 81.2 MPa. This is due to the formation of the structure of the biocomposite material, in which the strength is increased due to the mechanical interlocking of the stem particles.

The next stage of research concerns the determination of the compressive strength of biocomposite materials, which, after the main heat treatment of the composition in the mold, were additionally heated (additional heat treatment) in order to remove residual moisture. The compressive strength limit of such biocomposite materials, the compositions of which were not heated to remove moisture during preliminary heat treatment, is in the range of 17.5-25.5 MPa (Fig. 2).

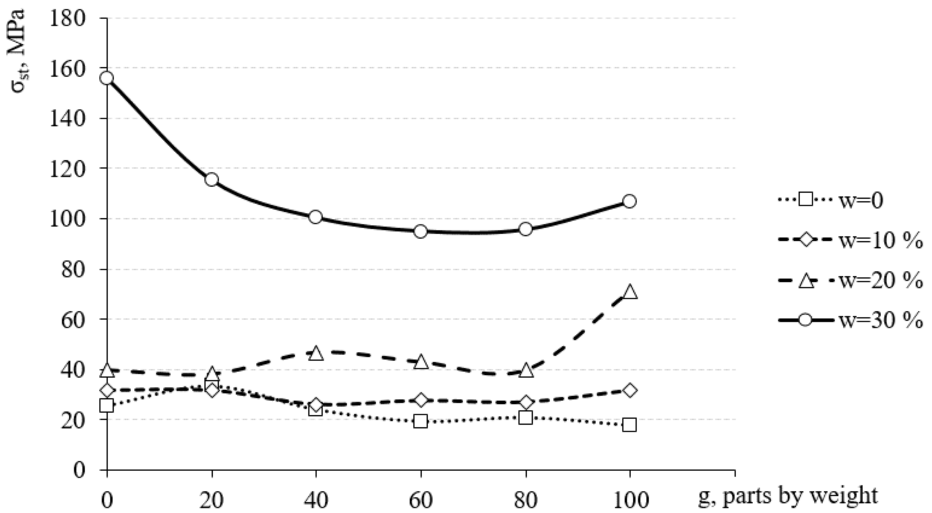

Fig. 2. **The influence of the content of chopped stalks of cereal crops on the compressive strength of biocomposite materials depending on the degree of moisture loss in the composition and additional heat treatment (50° C for 8 hours) of the biocomposite**

The obtained compressive strength values are higher by 52-56% compared to the strength of biocomposites that were not subjected to additional heat treatment. This is due to the removal of excess moisture from the composition. Excess moisture reduces the stiffness of the glutinous matrix and fillers of natural origin, which leads to a decrease in the resistance of the biocomposite material to the impact of static load.

Removal of 20% of moisture from the composition provides an increase of 31-45% in the compressive strength limit in the case of filling the system with chopped stalks in the amount of 60-100% compared to biocomposites from which the moisture was not removed. The increase in compressive strength is due to the higher content of chopped stalks, which are able to form a structure resistant to static loads.

Removing moisture from the composition in the amount of 20% allows to increase (by 32-43%) the compressive strength of biocomposites with a content of 40-80 parts by weight of filler compared to biocomposites in which 10% of moisture has been removed from the composition. The compressive strength limit increases significantly to 71 MPa for biocomposites with a content of 100% chopped stalks, which is due to the formation of physicochemical bonds between the stem particles and the biopolymer matrix. Removal of 20% of moisture from the composition ensures high stiffness of the glutinous matrix and strength of the stem particles.

The highest compressive strength (156 MPa) was obtained for biocomposites containing 100% wood flour (0% chopped stalks) with 30% moisture removal. The removal of moisture ensures the formation of a stable dense structure of the biocomposite material due to the lack of pressure of water molecules on the formation of physical and chemical bonds between the components of the biocomposite material. The limit of compressive strength of biocomposites containing a higher quantity of chopped stalks (60-80%) is reduced to 95 MPa. This is due to the sensitivity of cereal stalks to moisture loss, which leads to loss of elasticity and destruction under the influence of static load. Additional processing provides relaxation of residual stresses in the biocomposite material. This leads to an increase in compressive strength compared to biocomposites of a similar composition, for which no additional heat treatment was performed.

Conclusions and prospects for further research. Additional heat treatment provides relaxation of residual stresses, since the formation of biocomposite materials takes place in a compressed state at a temperature of 140° C. Biocomposite materials whose compositions have been heat treated to remove moisture in the maximum permissible amount of 30% have high compressive strength values. Removing moisture from the composition provides the highest compressive strength values of biocomposites compared to biocomposite materials whose compositions have an increased moisture content. The presence of additional moisture in the biocomposite material reduces the compressive strength limit, as the glutinous matrix dissolves and the bonds between the system components are destroyed.

Fillers can increase the compressive strength of biocomposites. For example, the compressive strength of biocomposites containing chopped stalks of grain crops in the optimal range of 40-60% is 130-136 MPa. This is achieved as a result of the formation of a dense structure of biocomposite material with a compact arrangement of filler particles in the glutinous matrix. The presence of a small amount of moisture contributes to the approach of macromolecules of the biopolymer matrix to the surface of the filler, which ensures the formation of additional physical and chemical bonds between active groups on the surface of the filler of natural origin and the glutinous binder.

In the future, it is planned to investigate the impact toughness of biocomposite materials in order to determine the effect of heat treatment on resistance to dynamic loads.

References

1. Contact-Rodrigo L., Ribes-Greus A., Imrie C.T. (2002). Thermal analysis of high-density polyethylene and low-density polyethylene with enhanced biodegradability. *Journal of Applied Polymer Science*, 86, 764-72.

2. Haque M., Alvarez V., Paci M., Mariano Pracella M. (2011). Processing, compatibilization and properties of ternary composites of Mater-Bi with polyolefins and hemp fibres. *Composites Part A: Applied Science and Manufacturing*, 42(12), 2060-2069.

3. Syamsir A., Mubin S.M., Nor N.M., Anggraini V., Nagappan S., Sofan A.M., Muda Z.C. (2020). Effect of combined drink cans and steel fibers on the impact resistance and mechanical properties of concrete. *Journal of mechanical engineering and sciences*,14, 6734-6742.

4. Pinho S.T., Iannucci L., Robinson P. (2006). Physically-based failure models and criteria for laminated fiber-reinforced composites with emphasis on fiber kinking. *Composites Part A: Applied Science and Manufacturing*, 37, 63-73.

5. Kashytskyi V.P., Sadova O.L., Vyshynskyi M.I., Myskovets S.V. (2023). Formation of glutinous biocomposite materials filled with chopped stalks of cereal crops. *Visnyk of Vinnytsia Politechnical Institute*, 1 (166), 65-71.

6. Mohanty A.K., Misra M., Drzal L.T. (2002). Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials word. *Journal of Polymers and the Environment*, 10(1/2), 19-26.

7. Joshi S.V., Drzal L.T., Mohanty A.K., Arora S. (2004). Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Composites Part A: Applied Science and Manufacturing*, 35, 371-376.

8. Rafiee K., Schritt H., Pleissner D., Kaur G., Brar S.K. (2021). Biodegradable green composites: it's never too late to mend. *Current Opinion in Green and Sustainable Chemistry*, 30, 100482.

9. Scaffaro R., Maio A., Gulino E.F., Pitarresi G. (2020). Lignocellulosic fillers and graphene nanoplatelets as hybrid reinforcement for polylactic acid: effect on mechanical properties and degradability. *Composites Science and Technology*, 190, 108008.

10. Nurazzi N.M., Asyraf M.R.M., Rayung M., Norrrahim M.N.F., Shazleen S.S., Rani M.S.A., Shafi A.R., Aisyah H.A., Radzi M.H.M., Sabaruddin F.A. (2021). Thermogravimetric analysis properties of cellulosic natural fiber polymer composites: Areview on influence of chemical treatments. *Polymers*, 13(16), 2710.

11. Kashytskyi V., Savchuk P., Sadova O., Mazurok V., Kostrytsya O. (2022). Formation of new biocomposites based on secondary raw materials obtained by recycling biocomposite products. *Naukovi notatki*, 74, 115-121.

12. Safri S., Sultan M., Jawaid M., Jayakrishna K. (2018). Impact behaviour of hybrid composites for structural applications: A review. *Composites Part B: Engineering*, 133, 112-121.

13. Kashytskyi V., Malets V., Sadova O., Shehynskyi V. (2022). Performance characteristics of glutin biocomposites filled with wood flour. *Naukovi notatki*, 73, 216-222.

14. Siracusa V., Blanco I. (2020) Bio-polyethylene (Bio-PE), bio-polypropylene (Bio-PP) and bio-poly(ethylene terephthalate) (Bio-PET): recent developments in bio-based polymers analogous to petroleum-derived ones for packaging and engineering applications. *Polymers*, 12(8), 1641.

15. Morreale M., Scaffaro R., Maio A., Mantia F.P. (2008). Effect of adding wood flour to the physical properties of a biodegradable polymer. *Composites: Part A*, 39, 503-513.

16. Kashytskyi V., Sadova O., Savchuk P., Malets V., Mazurok V., Myskovets S. (2021). Optimization of the composition and formation technology of biocomposites on the basis of starch binder. *Naukovi notatki*, 71, 353-359.