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МЕХАНІЧНІ ВЛАСТИВОСТІ БІОКОМПОЗИТНИХ МАТЕРІАЛІВ НА ОСНОВІ ЕПОКСИПОЛІМЕРНОЇ МАТРИЦІ

Визначено межу міцності при стисненні епоксикомпозитних матеріалів, які наповнені порошком деревного борошна або крохмалем. Визначено ефективність застосування порошку деревного борошна для формування епоксикомпозитів, що забезпечує вищі значення межі міцності при стисненні порівняно з міцністю при стисненні епоксикомпозитів з вмістом крохмалю. У випадку використання крохмалю відбувається підвищення адгезійної міцності епоксикомпозитів порівняно з ненаповненими епоксиполімерами. Підвищення адгезійної міцності компонентів епоксикомпозитного матеріалу відбувається за оптимального вмісту крохмалю в епоксиполімерній матриці та визначається адгезійним характером руйнування клейового з'єднання епоксикомпозитного матеріалу з поверхнею субстрату.

Ключові слова: органічний наповнювач; адгезія; міцність; твердість; напруження; пористість; покриття; структура.

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MECHANICAL PROPERTIES OF BIOCOMPOSITE MATERIALS BASED ON EPOXYPOLYMER MATRIX

The compressive strength limit of epoxy composite materials filled with wood flour powder or starch was determined. The effectiveness of the use of wood flour powder for the formation of epoxy composites was determined. The addition of wood flour powder provides higher compressive strength values of epoxy composites compared to the compressive strength of epoxy composites containing starch. In the case of using starch, the adhesive strength of epoxy composites increases compared to unfilled epoxy polymers. An increase in the adhesive strength of the components of the epoxy composite material occurs with the optimal content of starch in the epoxy polymer matrix. The optimal content of the filler is determined by the adhesive nature of the destruction of the adhesive connection of the epoxy composite material with the surface of the substrate.

Key words: organic filler; adhesion; strength; hardness; tension; porosity; coating; structure.

Formulation of the problem. Classic polymer composite materials consist of a synthetic polymer matrix and also contain dispersed, fibrous or sheet fillers. Fillers are divided according to their chemical composition into mineral, metal, polymer. In some cases, fillers are of natural origin (linen, cotton, paper). The optimal combination of mechanical properties of the polymer matrix and fillers made it possible to obtain a wide range of polymer composite materials that are widely used in various industries. The production of polymer composite products involves the use of technologies that have a harmful effect on the environment. Polymer composite products require disposal at the final stage of operation. Disposal consists in the processing of materials using recycling technologies or safe destruction with the formation of environmentally safe components. In the case of falling into landfills, polymer composite materials can be stored for a long time without destruction or can be destroyed with the release of harmful substances. Therefore, the use of polymer composite materials based on components of synthetic origin should be limited considering their dangerous impact on the environment, which requires a detailed analysis. This contributes to the development of new and promising directions for the creation of materials with the partial use of synthetic materials. At the same time, it is enough to replace fibrous synthetic fillers with natural components, which are able to provide satisfactory mechanical characteristics of the biocomposite product. This requires conducting theoretical and experimental studies to determine the nature of the interaction of components, which ensures a controlled process of forming the structure of biocomposite materials. As a result, biocomposite products with a complex of controlled mechanical and operational properties are obtained. Therefore, biocomposite materials and products based on them have the prospect of replacing classic polymer composite materials containing synthetic components with components of natural origin at the expense of.

Analysis of recent research and publications. Classic polymer composite materials have a synthetic polymer matrix and usually contain fibers of synthetic origin (carbon fibers, glass fibers, aramid fibers). Such materials have many advantages compared to unfilled polymers, which include higher mechanical characteristics and specific performance properties that each component does not have separately. The basis of polymer composite materials is a polymer matrix, which connects the particles or fibers of the filler and perceives and transmits the external load. As matrices, classic polymers based on thermoplastics (polyolefins, polyurethanes, polyesters, polyetheramides, polyvinyl alcohol) [1] and thermosets (epoxy, polyester, phenol-formaldehyde resins) are used. Thermosets have a highly cross-linked structure of polymers, which is formed under the influence of heat, pressure or light irradiation. Therefore,

this structure provides the thermosetting polymer with high mechanical characteristics (flexibility, strength and elasticity) [2, 3].

Due to the use of synthetic components, polymer composite materials have high weather resistance, resistance to chemicals and microorganisms. On the one hand, this increases the resource of their operation, but there are problems with their disposal after partial or complete destruction of polymer composite products. The main problem is the accumulation of such materials in the event that plastic products end up in a landfill. This leads over time to an increase in the area of such landfills, since polymer composite materials are stable and can remain in a landfill for hundreds or thousands of years [4]. At the same time, their slow destruction leads to the formation of toxic substances that are quite harmful to the environment, as well as human health.

This problem can be solved by replacing the synthetic filler with natural dispersed particles or fibers. The authors [5] use carbamide-formaldehyde resin to manufacture helmets based on bamboo fibers. The resistance of the biocomposite product to the influence of atmospheric factors, the strength in conditions of high or low temperature and the resistance to the influence of water of this biocomposite material increases as a result of the penetration of urea formaldehyde resin into the pores of bamboo fibers and the formation of chemical bonds between the resin and the filler. In addition, the crystallinity of the modified bamboo decreases from 36.72% to 34.09%, which improves the impact resistance of the biocomposite helmet.

The authors of [6, 7] developed polymer composite materials based on an epoxy matrix using fillers of natural origin (starch, discrete fibers of flax and technical hemp). It was established that the optimal starch content for massive epoxy composite products is 70 wt. parts. This provides an increase in the limit of compressive strength and impact toughness, which is associated with a compact arrangement of filler particles in the epoxy polymer binder and the formation of additional chemical bonds between functional groups of macromolecules of epoxy resin and active groups on the surface of the particles. Introduction to the composition of discrete flax fibers in the amount of 30 wt. of parts provides an increase in compressive strength by 18% compared to the content of 20 wt. parts. This is due to the formation of a homogeneous structure due to the ability of the fibers to be evenly distributed in the epoxy polymer matrix compared to the fibers of technical hemp, which are more rigid and form agglomerates with an oriented arrangement of fibers.

However, the main drawback of such polymer composites is the lack of complete biodegradability [8]. A simple solution to this problem is to replace classic synthetic polymers with biodegradable ones [9]. The prospect of higher economic attractiveness in the future of completely biological composites has appeared as a result of improving the properties of biologically based polymers. At the same time, the active use of biological polymers based on raw materials from renewable sources is not always advisable, especially in the short term. If biopolymer analogues are more expensive or their properties are worse, then it is better to use a resin made from a mixture of synthetic and biochemical substances. For example, the impact strength of petroleum-based epoxy resins can be significantly improved by mixing with epoxidized vegetable oils [10].

The use of natural fillers as reinforcing elements is limited due to their tendency to absorb water. This is due to the high content of cellulose, which has hydrophilic properties by nature. A decrease in mechanical characteristics and a change in the size of biocomposites occurs as a result of intensive water absorption. This leads to the appearance of microcracks in the biopolymer matrix and at the fiber-polymer interface [11-13].

The high hydrophilicity of natural fibers determines their tendency to absorb moisture from the environment. This can be a problem for many types of thermosetting resin systems because moisture acts as an inhibitor to the hardener in the structuring process of the thermosetting polymers. Residual moisture in the natural fiber can lead to the destruction of chemical bonds at the fiber-matrix interface, which leads to the formation of a composite structure with lower mechanical characteristics. This requires the operation of drying natural fillers [14] in the technological process of forming biocomposite products based on thermoset polymer matrices of synthetic origin [15].

Setting tasks. Determination of the compressive strength limit and adhesive strength of epoxy resin materials filled with finely dispersed powder of wood flour or starch.

Presentation of the main material. Epoxy composite samples were formed by pouring the composition into molds of a certain size. Dosing of components was carried out by the weight method according to the calculated content of the filler per 100 mass parts of the epoxy polymer binder. Mixing of the components of the composition was carried out using a mechanical method with a low speed of rotation of the blades in order to avoid heating the mixture. The compressive strength was determined according to

the ASTM D695 method "Compression testing of rigid plastics" on samples with a height of 15 mm and a diameter of 10 mm. The adhesive strength was determined by breaking the adhesive joint in the end part of cylindrical rods with a conical projection for self-centering. Heat treatment was carried out in a stepwise manner in order to reduce residual stresses in the epoxy composite material: 1 hour at a temperature of 70°C, 1 hour at a temperature of 100°C and 4 hours at a temperature of 140°C.

The compressive strength of epoxy polymer materials without filler is 74.7 MPa (Fig. 1). The compressive strength is reduced by 40-42% when 5-15 parts by weight of starch are added compared to unfilled epoxy polymer. This is due to the use of a filler that has a lower hardness compared to the hardness of the epoxy polymer. Starch particles are deformed under the influence of compression load, which leads to deformation and destruction of the epoxy polymer matrix. This is due to the growth of the specific load on the epoxy polymer matrix in the zone of interphase interaction of the components. In case of introduction of 20-60 parts by weight of filler, the strength limit of epoxy composites gradually decreases from 24.6 MPa to 14 MPa, which is 67-81% less compared to unfilled epoxy composites. The decrease in this characteristic is explained by the increase in the starch content, which, with the same binder content, causes a decrease in the wall thickness of the epoxy polymer matrix. This causes an increase in the specific load on the areas of the epoxy polymer matrix, which leads to their destruction.

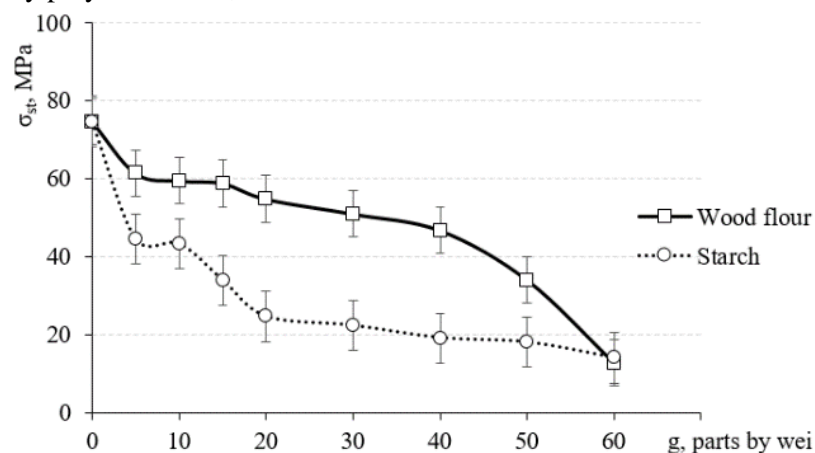


Fig. 1. The dependence of the compressive strength limit of biocomposites on the content of wood flour and starch in the epoxy polymer matrix

Epoxy composite materials containing particles of wood flour similarly resist compressive loading compared to epoxy composites filled with starch. The strength limit of epoxy composites decreases uniformly in the range from 61.4 MPa to 54.8 MPa in the case of the introduction of 5-20 parts by weight of wood flour particles compared to unfilled epoxy polymer. Such a decrease in characteristics by 18-26% is due to the use of a filler whose hardness and compressive strength are lower compared to the mechanical characteristics of epoxy polymers. The introduction of a filler in the amount of 30-60 parts by weight leads to a further decrease by 31-81% of the compressive strength of epoxy composites compared to epoxy polymer. A sharp decrease in this characteristic of epoxy composites containing wood flour particles is due to the formation of a heterogeneous structure compared to epoxy composites filled with starch. The sizes of starch particles are smaller, and their surface energy is lower compared to wood flour particles. Therefore, starch particles are compactly located and evenly distributed in the epoxy polymer matrix.

Strength compressed limit by 27-30% in the filling range of 5-15 parts by weight and by 47-56% in the filling range of 20-50 parts by weight epoxy composite materials filled with wood flour is higher. Higher compressive strength values of epoxy composites containing wood flour particles are due to the larger size of wood flour particles compared to starch particles. This provides a higher resistance of wood flour particles to the action of static load, which determines the higher strength of the walls of the epoxy polymer matrix. The difference in compressive strength decreases with increasing filler content, as the starch content in the epoxy polymer parts by weight matrix increases. Such epoxy composites with a high content of starch are not able to resist the compressive load, because the thin wall of the epoxy polymer matrix is rapidly destroyed. The strength limit of epoxy composites filled with wood flour and starch is the same and is 14.3 MPa at a higher filler content (60 parts by weight). This is due to the excess content of the filler, which is poorly wetted by the epoxy polymer binder. As a result, the amount of physical and chemical bonds formed is insufficient, which leads to a decrease in the ability of epoxy composites to resist static loads.

The adhesive strength of epoxy polymers without fillers is 24.3 MPa. A decrease in adhesive strength by 12-14% occurs when 5-10 parts by weight of wood flour particles are added compared to unfilled epoxy polymer (Fig. 2). This is due to the use of filler, which acts as a stress concentrator due to the irregular shape of the particles. This leads to the appearance of cracks and their instantaneous propagation in the zone of interphase interaction of the components. The adhesive strength of epoxy composites is sharply reduced by 40-54% in the case of the introduction of wood flour particles in the amount of 20-50 parts by weight compared to epoxy polymer. A further decrease in adhesive strength is associated with an increase in the filler content in the epoxy polymer matrix. An increase in the concentration of filler particles leads to an increase in the number of stress concentrators and an increase in the probability of crack initiation. The adhesive strength decreases to the lowest value (4 MPa) at the critical content of the filler (60 parts by weight), which indicates the impracticality of further research at a higher content of the filler.

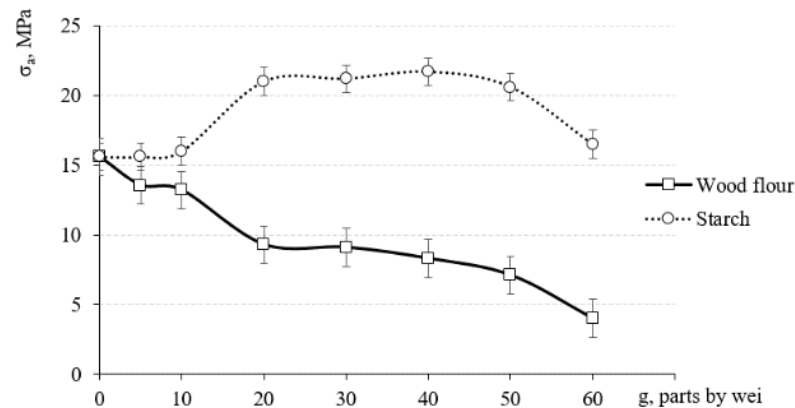


Fig. 2. The dependence of the adhesive strength of biocomposites on the content of wood flour and starch in the epoxy polymer matrix

The introduction of starch in the amount of 5-15 parts by weight allows to increase the adhesive strength of epoxy composites compared to epoxy polymer. The introduction of filler in the amount of 20-50 parts by weight leads to a 28-30% increase in the adhesive strength of epoxy composites compared to epoxy polymer, which is due to the compact arrangement of starch particles in the polymer matrix. Starch particles have the correct rounded shape, which ensures the formation of a homogeneous structure. An additional increase in the adhesive strength of the epoxy composite material occurs due to the formation of physical and chemical bonds between the active groups of the components. The adhesive strength of epoxy composites decreases by 24% with an increase in the starch content up to 60 parts by weight compared to the maximum values of adhesive strength of epoxy composites with an optimal filler content in the range of 20-50 parts by weight. A further increase in the starch content leads to the formation of a defective structure, since the wetting of the particles is complicated due to an insufficient amount of epoxy polymer binder.

The destruction of the adhesive seam, which is the investigated epoxy composite material, occurs as a result of stretching under the influence of normal stresses. The end surface of the steel rod is completely covered (Fig. 3, a) with an epoxy composite material containing starch particles in the amount of 30 parts by weight.

The part of the epoxy composite coating (silver color) was found on the end surface (Fig. 3, b) of the metal rod (brown color). The appearance of a brown color on the surface of the metal rod is due to the presence of a copper coating, which was applied as a result of the electrolytic deposition of copper ions in order to create contrast. The presence of an epoxy composite coating on one part of the metal rod and its absence on the other surface indicates the destruction of the adhesive seam at the interface "epoxy composite coating-metal surface of the rod". This indicates that the adhesion strength between the epoxy composite coating and the metal surface of the rod is lower than the adhesion strength between the starch particles and the epoxy polymer matrix. This is an additional fact that there is an increase in the adhesive strength of epoxy composites with a starch content of 30 parts by weight.

After the destruction of an epoxy composite adhesive joint (silver color) with a starch content of 60 parts by weight under the influence of normal stresses, the presence of an epoxy composite coating on two metal surfaces of the rods was revealed (Fig. 4).

As a result of visual analysis, it can be argued that the epoxy composite coating (silver color) occupies a larger surface area compared to the surface area of the metal rod (brown color). This indicates the cohesive nature of the failure of the epoxy composite material, since the adhesion between the metal surface of the rod and the epoxy composite material is higher than the adhesive strength between the starch particles and the epoxy polymer matrix.

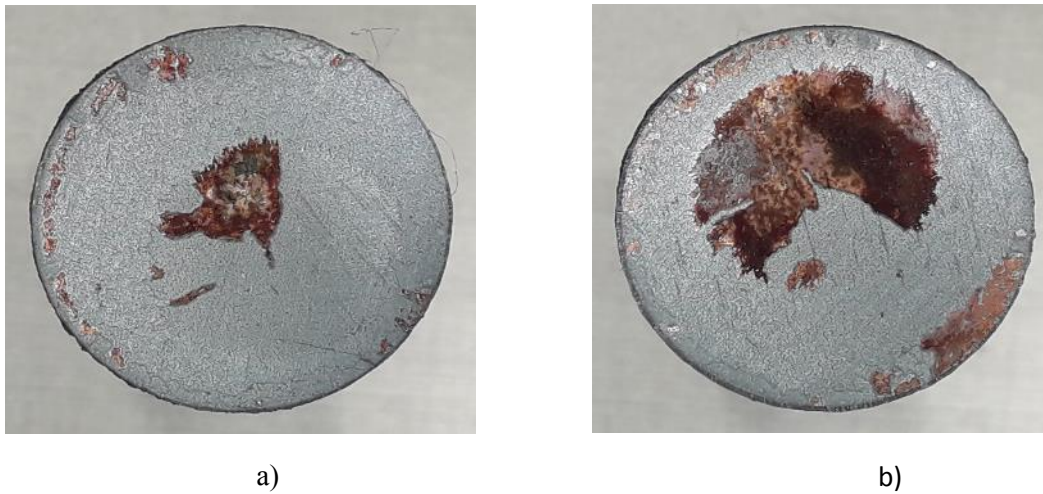


Fig. 3. The appearance of the surfaces of the adhesive joint after the destruction of the layer of epoxy composite material with a content of 30 parts by weight of starch

Therefore, the increased content of starch in the epoxy composite leads to a decrease in the adhesive strength of the material due to a decrease in the number of physical and chemical bonds between the components in the epoxy composite system and an increase in porosity.

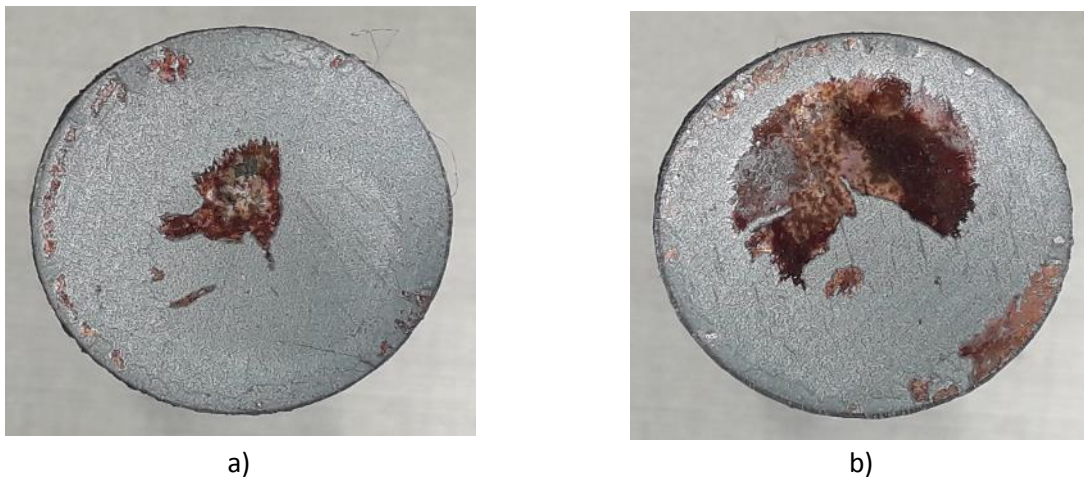


Fig. 4. The appearance of the surfaces of the adhesive joint after the destruction of the layer of epoxy composite material with a content of 60 parts by weight of starch

Conclusions and prospects for further research. The compressive strength of epoxy composite materials filled with wood flour particles is higher by 27-56% compared to epoxy composite materials filled with starch. This is due to the higher cohesive strength of wood flour particles compared to starch particles. In addition, wood flour particles have larger sizes, which determines their higher resistance to deformation under the influence of static load. At the same time, the higher strength of wood flour particles increases the resistance of the epoxy polymer matrix to deformation and destruction.

The introduction of starch powder in the optimal amount (20-50 parts by weight) into the composition of the epoxy composite material provides a 28-30% increase in adhesive strength compared to unfilled epoxy polymer. This is due to the formation of a homogeneous structure of the epoxy composite material, in which the filler particles are able to be placed evenly due to the correct shape and low coefficient of friction. Higher strength is provided by the formation of physical and chemical bonds between

the active groups of the components of the epoxy composite material, which is determined by the nature of the destruction of the adhesive joint. The destruction occurs at the interface between the metal surface of the substrate and the epoxy composite material at the optimal starch content, which indicates a higher adhesive strength between the starch particles and the epoxy polymer matrix.

In the future, it is planned to determine the mechanical characteristics and nature of structuring of epoxy composite materials containing particles of different chemical and granulometric composition.

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