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PROPERTIES AND FORMATION TECHNOLOGY OF GLUTINOUS BIOCOMPOSITE MATERIALS

ISBN 979-8-88955-328-1

DOI 10.46299/979-8-88955-328-1

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**PROPERTIES AND FORMATION TECHNOLOGY
OF GLUTINOUS BIOCOMPOSITE MATERIALS**

Monograph

2023

UDC 544.77.022:678.549

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Kashytskyi V.P., Sadova O.L., Malets V.M.. Properties and formation technology of
glutinous biocomposite materials. Monograph – Primedia eLaunch, Boston, USA, 2023. - 107 p.

ISBN 979-8-88955-328-1

DOI 10.46299/979-8-88955-328-1

The monograph presents the general characteristics and classification of biocomposite materials based on natural components, their advantages and scope of application are indicated. The mechanical properties of biocomposite materials based on a glutinous matrix and plant fillers were studied. The content of components was optimized. The formation modes of biocomposites with processing of the composition in physical fields were determined. The technology of recycling glutinous biocomposite products by thermo-mechanical processing of secondary raw materials has been developed.

The monograph is intended for specialists in materials science of polymer composites and biocomposite materials. It will also be useful for graduate students, students, materials scientists, technologists and engineers of technical specialties.

UDC 544.77.022:678.549

ISBN – 979-8-88955-328-1

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Content

Introduction.....	4
Chapter 1. New approaches in the development of innovative biocomposite materials based on eco-friendly raw materials.....	6
1.1. General characteristics of biocomposite materials.....	6
1.2. Technological features of manufacturing biocomposite products.....	20
1.3. Biodegradability and recycling of biocomposite products.....	24
1.4. Conclusions.....	27
Chapter 2. Characteristics of biocomposites components and research methods.	29
2.1. Characteristics and properties of biocomposites components.....	29
2.2. Research methods.....	34
2.3. Formation technology of biocomposite samples.....	37
Chapter 3. Biocomposites filled with wood flour.....	39
3.1. Development of forming technology of biocomposite products filled with wood flour.....	39
3.2. Operational properties of biocomposites filled with wood flour.....	45
Chapter 4. Optimizing the forming technology of biocomposites filled with chopped cereal stalks.....	51
Chapter 5. Features of modification of biocomposite materials.....	64
5.1. Modification of biocomposites filled with wood flour with sodium sulfate.....	64
5.2. Modification of biocomposites filled with coffee grounds with sodium sulfate.....	70
5.3 Modification of biocomposites filled with wood flour with polyvinyl acetate.....	79
Chapter 6. Development of recycling technology of biocomposite products.....	93
References.....	101

INTRODUCTION

Synthetic polymers and composite materials based on them are widely used in engineering for the manufacture of parts of machines and mechanisms, which are characterized by high manufacturability, corrosion resistance and specific strength. However, materials of this class are difficult to dispose of after use, so they mainly end up in landfills, which leads to environmental pollution and deterioration of environmental safety. In addition, the raw material base of synthetic polymers based on hydrocarbons is exhaustive, which in the future will lead to difficulties in obtaining raw materials and to an increase in the cost of products.

The modern development of biocomposite materials contributes to the gradual growth of demand in the market, because biocomposite materials are more practical, ecological, and cheaper than classical materials. The development of new biocomposite materials is taking place at a rapid pace, so their range is expanding on the market. Biocomposites are used in agriculture, horticulture, automotive industry, consumer electronics, toys, textiles and other industries. New biocomposite materials are manufactured using biotechnologies based on the development of biochemistry, microbiology and other sciences. The binding material in biocomposites is natural adhesive substances released from liquid or other plant material.

Biocomposites, in which the biopolymer matrix is reinforced with natural fibres, are a reliable and promising alternative to synthetic polymers. The effectiveness of such biocomposites depends on the properties of natural fibres used for reinforcement. Natural fillers are characterized by a high ability to recover, low density and cost, and are environmentally safe, biodegradable and distributed in nature. The biodegradability of plant fibres contributes to the preservation of the ecosystem, and their low cost and high productivity satisfy economic aspects.

Today, there are new approaches to the development of biocomposite materials for structural purposes, which are distinguished by high environmental safety and have high indicators of strength characteristics. The introduction of biocomposite materials based on components of natural origin allows solving the problem of disposal of used

biocomposite products or individual parts that are highly compatible with the environment, as they are able to break down under the influence of atmospheric factors and microorganisms into environmentally safe components. This will reduce the amount of use and reduce the harmful effects of synthetic polymers that are resistant to destruction and are a source of pollution.

The increase in demand for biocomposites raised the question of processing this material. The main methods of utilization and regeneration are the following ways of beneficial use of secondary biocomposite raw materials: burning for the purpose of obtaining energy; reuse; secondary processing. Incineration in incinerators is not a cost-effective method of disposal, as it represents a loss of valuable raw materials and the generation of waste.

The best ways to dispose of secondary biocomposite raw materials from an economic and ecological point of view are reuse and recycling into new types of materials and products. It is advisable to recycle biocomposites because the resources of many materials on the planet are limited and cannot be replenished in terms comparable to the time of human civilization. Once in the environment, materials usually become pollutants, so recycling will help solve some ecological problems. Improving recycling technologies and improving the properties of biocomposites after secondary processing will reduce the amount of biocomposite waste and involve the use of new raw materials.

The relevance of the development of composites based on components of natural origin is determined by the need to optimize the chemical composition and modes of the technological process of product formation, to study the peculiarities of the structure and properties of biocomposite materials that have high biodegradability and safety in the process of production, operation and disposal.

CHAPTER 1

NEW APPROACHES IN THE DEVELOPMENT OF INNOVATIVE BIOCOMPOSITE MATERIALS BASED ON ECO-FRIENDLY RAW MATERIALS

1.1. General characteristics of biocomposite materials

Environmental problems have caused the need to develop green composites as an alternative to synthetic polymers that do not degrade under the influence of atmospheric factors and microorganisms. Various biopolymers, including polysaccharides, polyesters, and proteins, are used as matrices in such composites. Such biopolymers have low mechanical and thermal properties, therefore, in order to improve these properties of biopolymer matrices, you can use organic fillers obtained from agricultural or wood processing industry waste. In most cases, special treatments and additives are used to prepare these green composites and overcome the problems associated with poor biopolymer-filler interactions [1].

Today, considerable attention from scientists in the field of polymer composite materials research is focused on the development of biodegradable materials that are capable of decomposition in the environment under the influence of biological and atmospheric factors. Due to their biocompatibility, non-toxicity and single use, biocomposites have a high potential for introduction into production in various industries, in particular as materials for the manufacture of medical device housings, furniture, building materials, packaging, and insulation. Such materials of organic origin create ample opportunities for the creation of a new class of environmentally safe materials, which will later replace plastics and other environmentally harmful materials around the world [2].

Biocomposite materials are made from raw materials of natural origin that do not contain mineral components, compared to materials such as carbon fibre and glass or epoxy resins. Therefore, biocomposites are more promising than their synthetic counterparts, as they do not require the use of fossil fuels or complex chemical reagents. Their ability to biodegrade allows products to be disposed of through recycling or

regular composting at the end of their useful life without harming the environment. At the same time, biocomposite products have satisfactory mechanical, chemical and operational properties compared to their synthetic counterparts.

Biocomposite materials (fibres of flax, hemp, wool, silk, bamboo, and wool) are made from raw materials from various natural sources, mainly of plant origin. At the same time, rubber, thermoplastic or thermoreactoplastic polymers are usually used as a matrix material for the formation of biocomposites [3, 4]. Plants are the most effective source of raw materials for the production of biocomposite fillers due to their high quality, quantity and availability. However, the physical and mechanical properties (thickness, solubility in water, and density) of plant materials differ significantly, which calls for experimental and theoretical studies to establish the nature and mechanism of interaction between fillers of natural origin and the polymer matrix. In addition, the ability to modify plant materials leads to changes in the chemical and physical properties of biocomposites and provides an increase in the degree of crystallization and polymerization of the biopolymer matrix, which expands the scope of application of biocomposite products.

According to the international classification, the spectrum of natural fibres is defined, which are divided into three main groups-vegetable, animal, and mineral origin (Figure 1.1). The fibres of bark, leaves, and wood are the most popular for reinforcing the biopolymer matrix. Bast fibres such as flax, hemp, jute, and kenaf are obtained from the stems of plants and are most often used as a reinforcing element because they have a known length, the highest strength and stiffness. Flax and hemp fibres are of particular importance in Europe, which are characterized by a developed raw material base due to the favourable climate in this region [5].

The advantages of reinforcing fibres of natural origin are renewable raw materials, low cost and availability. Also, the advantages of natural fibres are their low density, higher tensile strength and stiffness than glass fibres, as well as lower costs in the production process [6]. Composites from natural fibres are quite cost-effective, especially for the manufacture of structures, packaging, the interior of cars and railway cars, and instrument housings. Natural fibre has a hollow structure that provides high

insulation from noise and heat. Due to the structural features, natural fibres can be potentially suitable for replacing expensive glass fibre, which is used for the manufacture of products exposed to low loads.

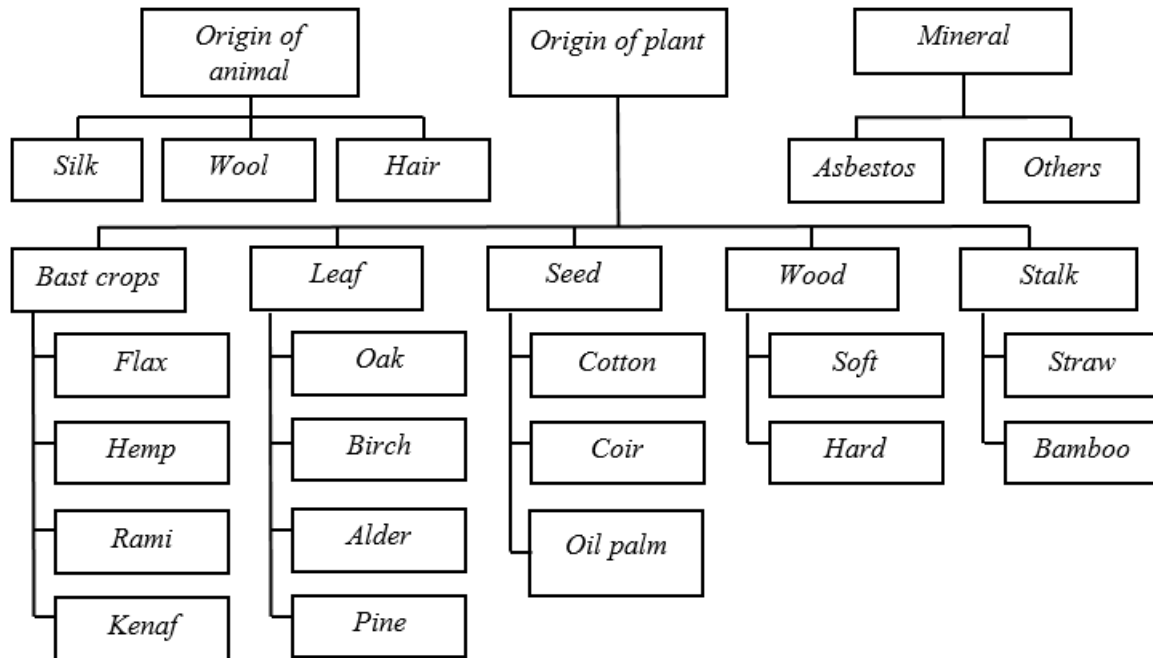


Figure 1.1. Classification of types of natural fibers

The paper [7] determined the highest tensile strength for biocomposite materials filled with 50-60% by mass fibres of flax, beetle, DPF and banana palms, which is 8-15 times higher than the strength of the material without filler. In the case of introducing fibres in the amount of 80 wt.%, the content of the matrix is insufficient, so the binder is not able to fill the gaps between the fibres and transfer the load, which leads to a significant deterioration of the tensile properties. For the hemp composite, the strength can be increased to 360-370 MPa in the case of an increase in the fibre content to 70%. The small diameter and solid fibres with high strength (700 MPa) provided a significant increase in the strength of the biocomposite. The moisture absorption of TPS/lignocellulosic fibre composites was found to be affected by fibre type and content. Increasing the fibre content and choosing a fibre with a high cellulose content improves the moisture resistance of the composites. In addition, the correct choice of the method

of surface treatment of the fibre significantly changes its water resistance. The thermal stability of TPS/lignocellulosic fibre composites improves with increasing fibre content. This is explained by the high thermal stability of cellulose compared to starch. In addition, the correct choice of the method of processing the surface of the fibre increases the thermal stability of the fibre itself and the resulting biocomposite. A hydrophobically modified starch or a hydrophobic coating can be applied to further improve moisture resistance. Starch fibre panels can be used to make decorative panels for residential buildings or cars.

Along with fibrous materials, the products of the woodworking industry are widely used for the manufacture of furniture and building materials. At the same time, most of the wood waste obtained as a result of the demolition of wooden buildings, massive deforestation and the manufacture of lumber is usually burned for disposal or energy purposes, which causes serious environmental problems. Basically, such waste is sawdust in the form of spherical or plate-shaped particles, which after additional processing can be successfully used as a filler for the production of biocomposite materials. Thus, there is a significant demand for the development of new technologies that could provide new ways of consuming unused waste from the production of lumber, as well as the production of wood-composite materials in a more efficient and environmentally safe way [8].

Wood-plastic composites (WPC) consist of short wood fibres (<1 mm long) or contain wood flour in thermoplastic polymer matrices, most commonly polypropylene (PP), polyethylene (PE), and polyvinyl chloride (PVC). These polymers are chosen for their low cost and low processing temperature, which minimizes the degradation of wood fibres. In many cases, the polymer matrix is modified to increase mechanical characteristics and improve aesthetic appearance. Wood flour is an attractive raw material because it has a high bulk density.

during formation and low cost, as it is a waste of sawmills. The wood content of WPC is usually 30-70% by weight, while typical wood species are used (fir, pine, spruce, maple, oak and beech).

Often, the materials are mixed in an extruder (twin-screw extruder), which has some advantages over planetary extruders. This allows extruding the composition directly into products of the desired profile, as well as providing thermoforming of parts. The wood fibres must be dried to a loss of 0.5% of water weight to ensure a high-quality finish.

At the stage of forming the composition mixture, it is necessary to include functional additives, such as lubricants, binders, dispersants, foaming agents, antioxidants, heat stabilizers, impact modifiers, UV stabilizers, pigments, and fungicides [9]. WPCs typically have good stiffness, strength and heat resistance, but low impact strength. Impact toughness can be improved by adding modifiers such as maleic anhydride (MAPP) or viscose fibres (10 wt.%).

Products based on WPC are used for the manufacture of building structures (flooring, railings), details of car interiors (door covers, shelves, housings, loudspeaker housings, etc.), industrial goods (pallets, boards) and consumer goods (furniture, flower pots, dishes, handles, outdoor furniture, garden tables, garden benches).

Not all plastic composites contain wood fibres. In the UK, polymer biocomposites are made from a blend of polyolefins with polystyrene added to improve properties and reinforced with flax fibres.

Natural fibres are inherently discontinuous, as they are randomly oriented after processing. It is known that high strength and stiffness of composites can be achieved as a result of using continuous, aligned reinforcing fibres. Aligned natural fibres can be combined with thermoplastic polymers in several ways. Woven or stitched fabrics can be impregnated with layers of thermoplastic in a press or vacuum chamber [10]. In laboratory studies, strands of natural fibres can be wound on a frame for unidirectional reinforcement and then combined with thermoplastic films before heating and pressing [11]. In all cases, it is necessary to limit the temperature and exposure at this temperature to prevent the degradation of natural fibres. Products that are formed by heating under a vacuum to reduce the effect of oxidation are of high quality. Thermoplastic pultrusion of natural fibre is also possible [12], although natural fibre materials must have sufficient strength to resist tearing during service.

The biopolymer matrix performs an important function to protect fibres from the destruction and degradation of biocomposites during the operation of products under the influence of atmospheric factors and mechanical damage and also ensures the transmission and redistribution of loads from physical fields on the fibres [13]. In addition, the biopolymer matrix should ensure high homogeneity of the material, the possibility of processing into products without decomposition and the separation of low molecular weight products. The defining and main property of such materials is biological harmlessness, that is, the absence of an irritating, toxic or carcinogenic effect on living organisms. Such biocomposite materials should have high technological characteristics with the use of relatively cheap methods of forming products. The availability of raw materials is of great importance since the cost of manufacturing biocomposite components affects the economic efficiency and profitability of biocomposite products [14].

Promising directions in the development of biodegradable polymer composites are composites reinforced with starch. Such materials have not been studied much, so they need the development of forming technology and the study of properties. Starch is an inexpensive biodegradable polymer with distinctive properties and some disadvantages. Blending with other polymers has led to the development of an improved composite material with more advanced properties and a variety of applications [15]. Starch is the most frequently researched material as an environmentally friendly polymer based on renewable plant material, fully biodegradable and cheap. For the production of polymers, starch from corn, rice, wheat, or potatoes are used, which is inexpensive and has an extensive raw material base [34]. Starch varieties suitable for the production of biopolymers are obtained as a result of selective breeding and have a high amylose content. Starch-based biopolymers are very sensitive to water, brittle and have low thermal stability, but these problems can be solved by hydrophobic modification (acetylation) and the use of plasticizers. As a result of starch acetylation, starch acetate is obtained, which has less brittleness and higher strength. Plasticization with polyalcohols ensures the formation of long alkyl chains, which improves water resistance, lowers the glass transition temperature and increases the technological

properties of starch [16]. The most common is the use of starch biopolymers for the production of packaging materials (trays, film).

Vegetable cellulose can be successfully used for the production of cellulosic plastics after the acetylation process. Cellulose, by its very nature, is a biodegradable and environmentally safe material and also belongs to the raw material base with a constantly renewable resource.

Biodegradable thermoplastic polyesters can be derived from fossil fuels or renewable sources. Polycaprolactone (PCL) is a polyester that is biodegradable, but derived from fossil petroleum, while polylactic acid (PLA) is a biodegradable polyester that is made from biological sources.

At the same time, it is necessary to define the difference between biodegradable polymers, because not all bio-based polymers are biodegradable. Bio-based polymers, which are made from natural products, are renewable raw materials, while biodegradable polymers can be broken down by microorganisms at the end of their life. There are also significant differences between biodegradable, biodegradable and compostable polymers.

Polymers that decompose into smaller molecules or fragments through chemical reactions that are initiated by heat or ultraviolet light belong to the group of decomposed. Biodegradable polymers can be converted by natural microorganisms (bacteria, fungi, or algae) into biomass, carbon dioxide and water, which are more environmentally friendly than polymers that decompose under the influence of physical fields. However, biodegradation can produce methane and the waste can contain toxins. Compostable polymers break down into products that support plant life and are toxin-free. In some cases, biodegradation or composting requires special environmental and technological conditions (certain types of bacteria, temperature, moisture), which can be achieved at industrial facilities.

Biodegradable films based on starch as a matrix were developed. Starch films were reinforced with wheat and corn husks [17]. The paper examines the influence of filler particle size on the microstructure and mechanical properties of starch-based films. It was recorded that the addition of filler increased the modulus, tensile strength and

impact strength of the starch matrix by improving its elongation capacity. Studies on the effect of water vapor transmission rate have shown that corn starch is more effective in reducing vapor permeability than wheat husk. Using scanning electron microscopy, a high degree of compatibility of both fillers with the matrix was recorded. All components are hydrophilic and exhibit polar properties. Observations using optical microscopy and X-Ray diffraction revealed that the processing conditions did not affect the structure and change in the geometric shape of the components. The components of the developed biocomposites are obtained from food resources, so the films can also be used for the production of edible packaging.

The main problems of the wide implementation of composites based on starch binder are short-term stability, low water resistance, deterioration of mechanical properties due to moisture absorption and relatively fast biodegradation [18]. In order to overcome these shortcomings, natural lignocellulosic fibres are widely used for reinforcing biocomposites, which allows for the improvement of the properties, in particular mechanical, of starch-based polymers. Compared to synthetic fibres, natural fibres are less dense, in addition to being completely biodegradable. Lignocellulosic fibres such as sisal, jute, kenaf, coir, wood, cellulose, bagasse, banana, orange, and flax have been studied to improve the properties of the starch-based matrix [19, 20].

For the formation of biocomposite materials, fibres based on recycled wood or waste paper and even by-products of food crops are also used [21]. The criteria for the selection of fibres are influenced by the significant values of tensile strength, stiffness, elongation at break, fibre-matrix adhesion, thermal stability, dynamic and long-term behaviour of the composite, as well as processing costs. Biocomposite manufacturing approaches are being established that involve wetting, mixing, or saturating the reinforcing fibres and matrix together, whereby the fibres and polymer matrix bond and form a solid structure through chemical and thermal reactions. In order to create functional materials intended for highly efficient applications, nanocellulose of natural origin was produced with appropriate physical and mechanical properties [22]. Technical hemp fibre composites work well in applications where weight reduction and increased stiffness are important.

Biocomposites based on the starch binder and wood flour modified with glutin solution have been developed. It was established that the optimal content of wood flour (65 parts by mass) and the increase in the content of the modifier contribute to the formation of a homogeneous dense structure of biocomposites, increasing their hardness and strength [23]. Therefore, biocomposite materials were developed based on a solution of glutin and dispersed fillers-waste of plant origin (coffee grounds with high particle dispersion, crushed dried leaves, coconut coir and stalks of grain crops). It was established that the highest compressive strength values (78.02 MPa) have biocomposites containing particles of cereal stems in the amount of 190 mass parts [24]. In [25], it was determined that increasing the exposure time of biocomposites based on a glutin solution to 5 hours at the first stage of heat treatment leads to a 2-2.2-fold decrease in compressive strength, since the formation of a porous structure of the biocomposite material with numerous delamination and macro defects due to mould leaks. Application after the first stage of heat treatment of an additional operation of pressing the composition in a heated state ensures the preservation of the integrity of the material. In the case of applying heat treatment at the first stage, within 3 hours, the compressive strength of the biocomposite material increases by 40%.

Chemically modified starch microparticles (CSM) are produced as a result of a chemical reaction with malic acid using the dry preparation method [26]. Composites were prepared using modified starch microparticles and various cellulosic materials as fillers in a glycerol plasticized corn matrix by casting. The water resistance of the surface of the composite materials was improved by adding cellulose fillers to the starch-based polymer matrix. Samples containing cellulosic fillers have higher tensile strength but lower elongation values compared to samples without fillers. Starch, which is reinforced with cellulose, is a typical example of a natural polymer composite. A relatively good tendency to dispersion and alignment of cellulose fillers in the composite material was recorded in the obtained biocomposites. This is ensured by a larger amount of thermoplastic starch by weight compared to the amount of cellulose filler by weight. The transparency of composite materials is reduced due to the addition of cellulose fillers in the plasticized starch-based polymer matrix. The tensile strength and Young's

modulus values are significantly related to the nature of the polymer matrix and the adhesion between the cellulosic fillers and the plasticized starch-based polymer matrix. All cellulosic fillers increased the tensile strength due to better distribution of the fillers, but reduced the flexibility of the starch polymer chains in the composites, which affected the elongation at break. Young's modulus values for composite samples are lower compared to samples containing pure cellulose. This fact may be related to the chemical similarity between starch and cellulose, which provides better interaction and the formation of more hydrogen bonds in the structure of the composite.

Composites based on modified starch were obtained by combining starch with sisal fibres to study the effect of cross-modification of starch on the mechanical properties of the developed biodegradable composites [27]. Mechanical test results showed that cross-modification of starch improved the viscosity of the biocomposites, while single-modification improved the tensile strength. Oxidized esterified starch composites have the highest ductility with improved elongation at break and 136.1% and 54.3% higher Young's modulus, respectively, compared to the natural starch composite. At the same time, the tensile strength of the composite based on esterified starch increased by 61.6%. Infrared spectroscopy showed that the modification of starch provided a change in the functional groups of starch, with the formation of strong hydrogen bonds. X-Ray diffraction analysis showed that the degree of crystallinity decreased after starch modification. Composites based on esterified starch have the lowest crystallinity, with a highly damaged structure. Scanning electron microscopy images showed that the esterified starch provides the formation of a cellular structure that allows the starch to be uniformly attached to the surface of the sisal fibres.

Much attention has been paid to environmentally safe materials from natural and renewable resources due to the growing level of ecological problems and the uncertainty of oil resources. Widespread use of biodegradable plastics and resources is seen as one of many strategic directions to reduce the impact of synthetic plastics on the environment. Biocomposites of starch and cellulosic fibers are constantly attracting interest as environmentally friendly materials and as biodegradable renewable resources for sustainable development. Composites were formed by solution casting from corn

starch using 0-15 wt.% microcellulose fibers as a filler [28]. It was determined that the higher fiber content increased the modulus of elasticity by 92% and the degradation temperature up to 355°C. Good adhesion between the matrix and fibers due to their chemical similarity was recorded by optical microscopy. The resulting biocomposites have much better water resistance and a more hydrophobic character than unfilled thermoplastic starch films. Biodegradation resistance studies confirmed that the resulting composites are environmentally safe materials that are suitable for various applications. Starch is one of the most widely used materials for the production of biodegradable plastics because it is naturally renewable, cheap and available. However, films derived from starch are brittle and difficult to process. Therefore, various plasticizers are usually added to the film-forming solution before forming and drying procedures to produce thermoplastic starch.

Glycerin, which today is in most cases a waste product of biofuel production, gives the best results in reducing the friction between starch molecules. It is possible to improve the properties of a film based on starch by reinforcing it with fillers. Therefore, there is a growing interest in the use of fillers and fibers, in particular cellulose fibers, as reinforcing elements in TPS matrices during the production of green composites. Cellulose fibers are obtained from various sources, such as kenaf fiber, jute, ramie, cellulose fibers from recycled paper, lignocellulosic fibers, cellulosic fibers from cellulose, and sisal-coir fibers.

The main advantages of such green composites are their high tensile strength due to the chemical compatibility between starch and cellulose, high resistance to water due to the hydrophobicity of the fibers, as well as the ability to biodegrade. The fibers provided greater thermal stability of the TPS matrix, which led to higher decomposition temperatures of the biocomposites. It was found that the addition of lignocellulosic fibers decreased the kinetics of water absorption, providing the lowest percentage of water absorption. The method of infrared spectroscopy revealed changes in the structure of starch upon addition of cellulose fibers. At the same time, the absorption peaks corresponding to hydroxyl groups are shifted to lower wave numbers, which indicates the existence of hydrogen interaction between the components. Biodegradability studies

revealed that the prepared samples were completely biodegradable and not harmful if released into the environment. The use of natural fibers as a filler in TPS is an interesting alternative for the production of low-cost and environmentally friendly composites for use as a commodity plastic or packaging material.

The paper [29] presents the characteristics and research results of the developed composite biofilms, which are made using wheat gluten and cellulose acetate phthalate. Biofilms act as barriers against moisture penetration and oxygen diffusion through the film. The films had different thickness and concentration of components, which made it possible to analyze the ability of the films to water vapor and oxygen permeability, solubility in water and acids, as well as mechanical properties. It was established that the developed mixture increases the characteristics of the film more than each of the individual components separately. A mixture with a 1:1 ratio of components has a higher permeability to water and oxygen. The biocomposite films were completely soluble in water and acid, except for the film with the highest gluten concentration, which was 50% soluble in water and acid. An increase of gluten concentration in composite films led to a decrease in tensile strength. No significant difference in elongation at break and thickness was found between the composite films. A mixture with a 1:1 ratio of components has a higher permeability to water and oxygen. The biocomposite films were completely soluble in water and acid, except for the film with the highest gluten concentration, which was 50% soluble in water and acid. An increase of gluten concentration in composite films led to a decrease in tensile strength. No significant difference in elongation at break and thickness was found between the composite films. The film was prepared from a solution of gluten (9.0 g/100 ml of solution), absolute ethanol (32.5 ml/100 ml of solution), glycerol (1.50 g/100 ml of solution), distilled water and ammonium hydroxide under the condition of acidity to pH 10. All components were mixed on a magnetic stirrer until the temperature of the mixture reached 70°C. The solution was centrifuged for 6 min at room temperature. The film-forming solution was poured and evenly distributed over the Teflon-coated glass surface and dried at room temperature for 24 hours. Composite films of wheat gluten and cellulose acetate phthalate have lower vapor permeability than films of gluten or cellulose. This indicates

the possibility of forming films with high vapor barrier capacity. As the concentration of gluten in composite films increases, the solubility in acid and water decreases, as well as the mechanical strength of the films.

Poly(lactic acid) (PLA) is a thermoplastic biopolymer obtained by fermentation by microorganisms that feed on simple sugars or as a result of the conversion of starch. It has been used for many years in the biomedical sector to make drugs but has recently become economically feasible for wider use [30]. PLA is used mainly for packaging in the food industry (trays, films, cups, and bottles), but there are options to incorporate PLA to make textiles and fibre filling for pillows.

Lignin is a natural matrix material that binds strong and rigid cellulose fibres together (natural wood). After chemical separation, a thermoplastic-type polymer is obtained, which can be heated and used to modify synthetic thermoplastics [31]. Lignin can be in the form of a brown powder, but more often a sticky mixture with a wide range of molecular weights. It is a by-product of the paper and wood processing industries, but with massive deforestation, the commercialization of other wood products and technologies is increasing, and lignin can become an important raw material for the production of many chemicals. Today, bio-based polymers tend to cost more than synthetic polymers, but prices for synthetic polymer-based products are expected to rise in the future due to declining crude oil reserves.

A wide range of vegetable oils can be converted into more active bio-resins. Vegetable oils contain complex esters of various fatty acids, which can be functionalized with the help of reactive groups (hydroxyl, carboxyl, amine, and epoxide), which are capable of forming chemical bonds and forming rigid polymers [32]. Synthetic resins require chemical cross-linkers with various isocyanates (amines, polyols, and poly carboxylates), so acids are used in most cases. Current research is focused on finding isocyanates from biological sources.

The choice of raw materials, as a rule, is carried out according to the geographical principle, taking into account the peculiarities of growing agricultural crops. Therefore, attention is paid to soybeans in the USA, while interest in Europe is focused on obtaining oil from linseed, rapeseed, and sunflower.

Thermosetting bioresins are developed with appropriate technological characteristics and mechanical properties. There were soy resins

Modern technologies are capable of converting plant oil into resin precursors, which can be polymerized with a catalyst and heat. The technology involves using the reactivity of ozone to form double bonds in the oil, thus forming oxygen bonds that can be converted into reactive groups. Resins can be used as a sustainable alternative to petrochemical-based synthetic resins, phenol-formaldehyde and isocyanates that are hazardous to health, for example, in wood-based products such as MDF. Today, the industry has developed a technology for obtaining resin, which contains 95% vegetable oil and is polymerized with the help of ultraviolet sources.

Cashew Nut Shell Liquid (CNSL) is another type of natural oil that can be successfully processed into thermosetting resins. Cardanol is an alkyl phenolic product obtained by vacuum distillation of CNSL, which is reactive due to double bonds [59]. Numerous cashew nuts are grown in Africa, India, and Brazil. This means that the price of CNSL is lower than similar synthetic phenolic compounds, although its chemical composition is significantly different.

The authors of the paper [33] developed an energy-efficient and environmentally friendly composite material for construction purposes based on rapeseed straw and environmentally friendly glue. Bone glue with the addition of sodium lignosulfonate was used as a biopolymer matrix. Rapeseed straw particles are modified by treatment with water and sodium hydroxide. As a result of experimental studies, it was established that surface treatment with water or sodium hydroxide improves adhesion between rapeseed straw and bone glue. This provides an increase in the volume and matrix density of the developed biocomposite materials compared to the reference material. The best mechanical properties were obtained for samples treated with water. It was found that treatment with sodium hydroxide negatively affects the sorption isotherms and causes a greater degree of swelling compared to other composites. At the same time, the treatment of the straw surface does not affect the thermophysical properties of biocomposites and the ability to diffuse water vapour. Significant swelling of all the developed composites under the condition of reaching a relative moisture above 75%

limits their practical application. In this case, it is assumed that they will be used in dry environments, as a rule, for cladding and insulation in construction or for the manufacture of packaging.

1.2. Technological features of manufacturing biocomposite products

An important technological stage in the process of manufacturing products based on natural fibres is the method, period of collection and processing of raw materials, which affects the reduction of the duration of preparation of the moulding mixture and the reduction of costs associated with additional processing of fibres. In addition, the mechanical characteristics of biocomposite materials and the methods of their formation depend on the chemical composition and properties of the matrix, the dispersion of fillers and their porosity [34-37].

The most suitable methods of forming biocomposite products are injection moulding and pressing, the main advantage of which is ensuring high manufacturability, although the fibre can be damaged during the technological process. At the same time, it is necessary to analyse the technological factors and features of the technological process before deciding to use such a method. In particular, it is necessary to take into account the properties of the machine (composition temperature, coolant temperature, compactor pressure, compression force and composition supply pressure), moulding mode parameters (melting temperature of the biopolymer binder, cooling temperature, melt pressure, cooling time, material flow rate and speed feed), as well as quality indicators (sizes of parts, presence and sizes of defects, appearance and strength, surface texture and aesthetic appearance). Compression moulding is used for the production of complex biocomposite parts, as part quality requirements are an important factor in choosing such a method, which is usually intermittent, is used for the production of small volumes of materials, and the raw materials can be supplied in the form of sheets, composite pellets and prepregs [38].

Products based on biocomposites containing natural fibres are formed by injection moulding or extrusion methods. At the same time, starch-based biocomposite

compositions containing 50% of natural fibres (hemp, flax, or wood) are processed by injection moulding, and in the case of introducing fibres in the amount of 60-70%, the extrusion method is used. Bio-based thermoplastic polymers such as PLA (poly lactic acid), starch and lignin are used as a matrix, which, in combination with natural fibres, provide increased stiffness and thermal stability of biocomposites. The process of forming products based on a matrix of poly lactic acid and flax fibres takes place using a twin-screw extruder, with heating of the composition to a temperature of 180° C, a pressure of 43 bar and the presence of a vacuum chamber to remove residual moisture. In the case of forming products by injection moulding, the optimal melt temperature is 180-200 °C, pressure 50 bar, melt flow rate 100-180 mm/s, and mould temperature 25-30 °C [39].

In the process of developing a technology for the formation of biocomposites based on lignin powder with a content of 10-45% of flax fibres, it was established that it is advisable to subject the composition to agglomeration to obtain granules by pressing [40]. Such a composition can be moulded under pressure at a temperature of 140-160 °C, which makes it possible to manufacture complex parts that are similar in properties and appearance to wood. Products containing fibrous fillers in the form of fabrics have better mechanical properties compared to reinforcement with short and randomly oriented fibres.

Promising biocomposites based on polyfurfuryl alcohol (PFA) were developed for the manufacture of car door panels by the press moulding method, which consisted in spraying furan resin on a sheet filler made of natural fibre, followed by moulding under a hot press at a temperature of 180 °C for 60 s [41]. Compositions based on furan resin containing natural fibres are advisable to be formed by hot compression, which allows obtaining volumetric products or sheet structures with high fire resistance, which makes them suitable for use in electrical engineering and the automotive industry.

Less common methods of manufacturing biocomposite products are pultrusion and manual laying. Pultrusion involves the process of drawing reinforcing fibres through a bath, where they are permeated by a binder, and then through a heated matrix, resulting in a continuous composite profile. This method is used for the production of

biocomposites based on natural fibres of flax, hemp and wool, jute fibres, jute, wood and starch, which ensures an increase in the strength of biocomposites, improvement of operational properties due to better impregnation, distribution, and alignment of reinforcing fibres [42].

The method of manual teaching is the oldest and simplest technology for forming biocomposite structures, which requires a minimal set of tools, but requires highly qualified personnel. At the same time, the mechanical characteristics and operational properties of the finished product will differ within the same batch, although they are made of the same materials and composition, which is associated with the use of human skills, the presence of defects or heterogeneous inclusions [43].

Recently, gluten-based solid biocomposites have attracted attention because the glassy gluten matrix has properties comparable to epoxy resin. The paper [44] proposed the introduction of a wet method of forming biocomposites using liquid compared to a dry method of forming composites filled with fibres. In the wet method, an ethanol solution is used to create a suspension and partially dissolve the original or crushed gluten particles. Fibres are subsequently immersed in the resulting solution. Drying of impregnated modified fibrous mats, obtained by the dry or wet method, leads to the preparation of prepregs, the layers of which are formed by compression into composites without the need to use any additional solvents or plasticizers. Gluten composites that are made by the wet process give much higher strength than any of the dry methods. The use of aqueous ethanol helps to dissolve part of the gluten (gliadin fraction) and leads to good wetting of the matrix between the fibres.

The introduction of the optimal content of wood flour into the composition of the biocomposite formed in the mould made it possible to obtain samples of a cylindrical shape without delamination and structural defects due to the application of a uniaxial compression load [45]. The work investigated the effect of wood flour on the viscosity of compositions based on starch gel and determined the optimal content of an aqueous solution of gluten in the composition, which ensured an increase in the hardness of biocomposite materials. The authors of the paper developed a technology for obtaining a starch gel and an aqueous solution of gluten, as well as optimized the mode of

formation of biocomposites under the influence of thermomechanical treatment with subsequent heat treatment of biocomposite samples, which ensured the formation of a dense and homogeneous structure of biocomposites. It was found that at the optimal content of the modifier (glutin solution) 70 wt. h. a homogeneous and dense structure of the biocomposite material is formed.

The work [46] presents the results of the analysis of the composition and technology of forming biocomposite materials based on an adhesive substance (glutin) and dispersed fillers obtained as a result of processing or processing secondary raw materials of plant origin. We used powders obtained by processing coffee grounds with high particle dispersion, mechanically crushed dried leaves, coconut coir, and stalks of grain crops. The content of fillers in biocomposite materials varied within 80-130 wt. h., which corresponded to the optimal content of particles in the biopolymer matrix. The samples were formed by combining the bone glue solution with the processed filler as a result of mechanical mixing of the components and subsequent pressing in a press. Ensuring the homogeneity and integrity of the biopolymer matrix occurs due to the staged mode of heat treatment of biocomposite materials. The optimal content of fillers is determined based on the results of the analysis of experimental studies of the compressive strength of cylindrical samples. It was established that the highest compressive strength values (78.02 MPa) have biocomposite materials containing particles of cereal stems in the amount of 190 wt. h. Biocomposite materials, which are filled with particles of crushed dried leaves, have the largest number of macroscopic defects after heat treatment. Numerous pores and cracks were found in these samples. Biocomposites filled with particles of crushed stalks of cereal crops have the least number of defects, which is confirmed by the obtained values of the compressive strength limit. The developed biocomposite materials can be used for the production of furniture and floor elements, vehicle interior decoration details, containers, and instrument housings.

1.3. Biodegradability and recycling of biocomposite products

During the processing of plant raw materials, an important factor is the development of waste-free technologies. Currently, the almost universal use of traditional, sometimes outdated, technologies leads to the accumulation of a large mass of waste from the processing of various bio-raw materials [47]. The future expansion of the directions of practical use of waste is inextricably linked to a comprehensive approach to recycling, which is based on the optimal use of their capabilities as a valuable raw material source in combination with scientifically based technological solutions [48, 49].

Now more and more attention is being paid to the problem of creating biodegradable polymer materials to reduce the ecological burden on the environment. The development and research of such materials are one of the priority directions of the development of science. Today, there are several scientific directions in the field of creating biodegradable polymer materials, which are engaged in the research of biopolymers and biocomposites based on natural and synthetic polymers, as well as the modification of synthetic polymer compositions to accelerate the destruction of the polymer matrix [50].

The most effective and widespread way to ensure biological degradation is the introduction of various natural fillers into the polymer composition, which are a nutrient medium for microorganisms, as well as additives that accelerate the destruction of the polymer material. Contrary to the fact that there is a large number of works dedicated to the creation of biocomposite materials, which describe the methods of obtaining them and the areas of application, the creation of new materials is an urgent task of modern materials science [51].

In the last decade, many countries of the world introduced restrictions and bans on the use of polymer packaging. As a result, technologies for creating more ecological packaging appeared. Today, biodegradable materials, more precisely biodegradable plastics, are recognized as the most effective means for the production of safe bags, films, and other plastic products [52-57].

Biocomposite materials, based on components of natural origin, have significant advantages compared to synthetic polymers and polymer composite materials, as they have a developed raw material base, are characterized by renewable resources, as well as environmental safety in the manufacturing process. On their basis, elements of device housings, sports equipment, containers, wood-polymer floor boards and plinths are made, which indicates a high potential for the realization of products based on biocomposite materials. Taking into account the life cycle of products, which includes the stage of disposal of products, biocomposite materials have proven themselves as environmentally safe products that, under the influence of natural factors, are able to decompose into environmentally safe components. As a result, the problem of energy-consuming waste processing and avoiding the appearance of harmful substances disappears.

This indicates the expediency of obtaining secondary raw materials through the processing of biocomposite products, which will allow full use of such raw materials in the further technological process of forming new products, as well as saving natural resources, expanding the raw material base, reducing the costs of recycling products and reducing the volume of landfills. The process of obtaining high-quality secondary raw materials requires the development of technology for grinding products, separating and preparing components for the formation of new products, as well as studying the processes of structuring and properties of products based on secondary raw materials, with the condition that such properties will ensure high values of physical, mechanical and operational characteristics.

Recycled biocomposites have attracted the wide attention of scientists and manufacturers due to their significantly improved physico-mechanical, thermal and rheological properties compared to conventional materials, as well as their potential for commercialization and absence of waste [58-60]. Secondary raw materials are obtained by recycling biocomposites containing textiles, cellulose and paper, wood, rubber and plastic, which have significant potential as reinforcing materials in composites because they are non-toxic, inexpensive, biodegradable, cost-effective and available in large quantities. Recycled plastic biocomposites are now being used as additives in a wide

range of materials due to their advantages over petroleum-based materials, as they have exceptional sustainable and biodegradable properties compared to conventional materials such as polymers and composites. New biocomposites are made from recycled plastics, including thermoplastics, thermoplastics, rubber, and foam. The significant potential of biocomposites is revealed by taking into account the industrial applications of recycled plastics, due to their low cost, recyclability and biodegradability, as well as their use in the automotive, construction and packaging industries.

Given the ability to biodegrade and recycle, biodegradable plastic contains organic carbon that can be converted into biomass, water, carbon dioxide, or methane by natural microorganisms such as bacteria and fungi within a time frame that meets the environmental conditions of the disposal method [61]. The biodegradability of composites is determined by the degree of biodegradability of their components, and if plant fibres demonstrate inherent biodegradability, then not all biological plastics can be defined as biodegradable. So, in particular, biocomposites based on poly lactic acid belong to the compostable category [62]. At the same time, the rate of degradation is mainly determined by the chemical basis of both the matrix and the fibre, which can be predicted by analysing their chemical composition: the presence of natural fibres, cellulose, and hemicellulose. The presence of polar groups in cellulose and hemicellulose cause biological degradation by creating a moist environment that favours the growth of microorganisms. Fibres are also susceptible to different types of degradation, such as UV and oxidative-thermal degradation due to lignin content, as well as thermal degradation due to hemicellulose. The degradation of environmentally friendly composites is also influenced by environmental factors to which the material is exposed [63]. Moisture, UV radiation, temperature, and the activity of microorganisms actively affect interfacial adhesion, causing micro- and macrocracks in the material, and accelerating the biodegradation of the composite. Currently, the recycling of bioplastics is difficult because the necessary infrastructure is not widely available, and the addition of fibres can prevent the reprocessing of the composite, as is the case with synthetic composites that are reinforced with glass fibres.

The authors of the work [64] considered the expediency of textile fabric waste processing for the development of biocomposite materials. This waste is ground to obtain a loose fibrous material, which is converted into a non-woven fabric or a twisted strand for the production of three-dimensional woven biocomposite blanks [65, 66]. In the case of using non-woven blanks, the canvases are made by combining polypropylene with cotton filler in different proportions. As the percentage of polypropylene fibres in the web increases, the mechanical properties of the composite generally improve. As a result of the study of the mechanical properties of the biocomposite material in conditions of high moisture, no significant changes in the value values were found [67]. At the same time, biocomposites, which are reinforced with a woven cloth made using yarn from secondary fibres and yarn from natural cotton, do not have a significant difference in mechanical and thermal characteristics.

The paper [68] considered the processing process of biocomposites based on soybean oil epoxide acrylate (AESO) as a matrix and sisal particles (SP) as a filler in an organic solvent environment, which is recommended by safety, health and environmental criteria. Solvent treatment involved breaking down the resin matrix and recovering the jute fabric, which was then reused to make new biocomposites. At the same time, the hardness values of the secondary composite were lower by 4%, the tensile strength varied depending on the composition, and the water absorption was significantly reduced in the range of 22-51%. Increased resistance to water absorption expands the field of application of biocomposites based on secondary raw materials in the field of transportation, packaging, and furniture.

1.4. Conclusions

The widespread use of biocomposite materials is due to problems related to environmental safety and exhaustion of raw materials. The use of biopolymer matrices and fillers based on animal or plant origin provides a solution to the specified problems. Biocomposite materials have a great prospect of implementation for the manufacture of structural or decorative products. However, now biocomposites have significantly worse

physical, mechanical and operational properties compared to polymer composites based on synthetic polymers and mineral or metal fillers.

The study of the structure, the nature of the interaction, the influence of technological factors made it possible to significantly improve the mechanical characteristics of biocomposites, which requires conducting scientific research to determine the optimal content of fillers and modifiers. The use of modifying additives is due to a change in the rheological properties of biopolymer solutions and the formation of a polymer grid with specified parameters, which increases the resistance of biocomposites to the influence of external factors. The introduction of modifying additives leads to a change in the mode of formation of biocomposite products, which requires conducting experimental studies to determine the influence of technological factors on the mechanical characteristics of biocomposite materials.

CHAPTER 2

CHARACTERISTICS OF BIOCOMPOSITES COMPONENTS AND RESEARCH METHODS

2.1. Characteristics and properties of biocomposites components

Characteristics of bone glue. Organic glue made from natural polymers. These are products of bone and soft connective tissue processing. Bone glue (Figure 2.1) belongs to the group of collagen or glutinous glues. Collagen is a strong natural polymer, a fibrillar protein, which is the basis of the connective tissues of organisms. Collagen found in the tendons, skin, muscles and bones of animals. When collagen is heated in water, it changes into the form of another compound – glutin (gelatin). Glutin properties: it swells in cold water, melts during heating, and turns into an elastic gel mass after cooling.



Figure 2.1. General appearance of bone glue

The quality of solid bone glue (Table 2.1) depends on its ability to glue and strength according to the ultimate shear stress of glued material samples, which is from 4 kPa to 10 kPa. The quality also depends on the moisture content, which should not exceed 17%.

The ash content of solid glue is 2.0-3.5%, the fat content is 0.3-0.5% to the dry residue, pH 5.5-7.5.

Table 2.1.

Physico-chemical characteristics of bone glue

Characteristics	Value
Appearance	Granules, grains, powdery particles, adhesive jelly
Color	From light yellow to dark brown
Particle size:	
granulated	2-5 mm
scaly, no more	0.5 mm
chopped, no more	3 mm
Mass fraction of moisture, %, not more than:	
granulated	17
scaly	8
shredded material	11
Bonding strength of wood, MPa	7.5-10
Mass fraction of total fat, %	3.0
Resistance of the solution against rotting, days	to 6
Foaming, cm ³	from 20-50

The method of preparing glutinous glue: granules of dry glue are placed in cold water. In water, the glue swells, absorbing it in an amount that exceeds its own weight and forms a jelly. The jelly is loaded into the container and slowly heated. The glue begins to melt at a temperature of 35-40 °C. Then the temperature is raised to 60-80 °C, at which the glue turns into a homogeneous liquid. The duration of boiling the glue should not exceed 2 hours to prevent deterioration of properties. The capacity for melting the glue is usually water or electrically heated.

Glutinous glues are environmentally friendly materials, but they are not moisture-resistant or fungus-resistant. Under normal conditions and wood moisture content of 12%, the strength of the glue joint can exceed the strength of the glued wood. Depending on the moisture of the air, bone glue can evaporate or absorb moisture. Frequent changes in moisture over time lead to a weakening of the adhesive layer. However, not only bone, but also any other glues are subject to aging. As you know, all antique furniture and musical instruments made using glutinous glues and serve, under normal use, for 150 years or more without destruction. It is recommended applying the glue on the gluing surface in a hot form. The working temperature of the solution for bone glue should be 40-60 °C.

Characteristics of wood flour powder. Wood flour is a powder consisting of small wood particles of arbitrary shapes (Figure 2.2), which are obtained specially in the process of grinding wood of hard and soft deciduous and coniferous species.



Figure 2.2. Appearance of wood flour powder

To obtain wood flour, pieces of waste from forestry and woodworking industries (sawdust and technological chips) are used. Often, other types of plant raw materials (various types of straw and stalks, grain husks, nut shells, cardboard waste) are used as raw materials for the production of flour. Flour from the shell of nuts (almond, walnut, forest, coconut, peanut) is also used in the world. This flour makes it possible to obtain materials with higher hardness, moisture resistance and electrical insulating properties.

The color of wood flour depends on the type of wood. The color of the flour can be from light beige to dark brown. The shape of the wood flour particles depends on the structure of the wood and the technological process of grinding the particles in the working bodies of the mills during random multi-sided impacts (compression, shear, impacts and collisions).

The fractional composition of wood flour depends on the method of grinding and particle classification (centrifugal, sieve, etc.). The properties of wood flour particles are determined by the type of wood, age and location of the particle in the trunk. The density of wood is highly dependent on moisture. For example, for dry wood flour from spruce, the density is 0.42 g/cm^3 , and at 8% moisture is 0.437 g/cm^3 ; for dry wood flour from pine 0.47 g/cm^3 , at 8% moisture is 0.491 g/cm^3 .

The bulk density of wood flour depends on many factors (moisture, size and shape of particles, wood species). The bulk density of wood is $100\text{-}220 \text{ kg/m}^3$; the normative value for flour grades 120-180 is $100\text{-}140 \text{ kg/m}^3$. Wood during the production of wood flour practically does not undergo chemical transformations. The chemical composition of wood flour corresponds to the composition of the original wood. Therefore, wood flour can be considered a natural material.

The fibrous structure of wood particles is porous and heterogeneous. The structure contains capillaries (open and clogged), fibrils and interfibrillar space. Impregnation of fibrous particles with binder occurs through the end surfaces. The binder penetrates into the space between particles, interfibrillar space and into capillaries (open). The possibility of penetration of the binder into the capillaries and interfibrillar space is determined by the ratio of the sizes of the elements of the particles and molecules of the composition, as well as the presence of moisture in the elements of the particles. The following dimensions are typical for wood flour particles: length $0.1\text{-}2.0 \text{ mm}$, width and thickness less than 0.25 mm , capillary diameter is 33 microns for spruce and pine flour particles, 41 microns for fir. The main disadvantages of wood flour are low moisture, heat and chemical resistance.

Moisture is an important indicator for wood flour particles. Particle sizes can increase significantly with increased moisture content. Moisture is in the capillaries and interfibrillar

space, which usually requires thorough drying of the filler before combining with the binder. Moisture according to the standard should be no more than 8%. For the production of thermoplastic biocomposites, the moisture content of flour should be less than 1%. The moisture content of wood flour for the production of phenoplasts should not be less than 3.0%.

Characteristics of coffee grounds. Coffee grounds (Figure 2.3) are waste from the preparation of ground coffee. Waste is used mainly in the household and in the economy:

- for making reusable dishes;
- fertilizer for flowers and plants due to the high content of nitrogen, phosphorus, potassium and other minerals;
- in dried form can be used as a secondary fuel.

Raw coffee beans, based on dry matter, contain 32-36% of extractive substances, which are stably stored for seven years or more under normal storage conditions. The dry matter of raw coffee includes the following main components, %: caffeine – 0.7-2.5; protein substances – 9-19.2; fat – 9.4-18; monosaccharides – 0.17-0.65; sucrose – 4.2-11.8; fiber – 32.5-33.5; pentosans – 5-7; tannins – 8.7-11.9; mineral substances – 3.7-4.5; organic acids: chlorogenic – 4-10.9, citric - 0.3, tartaric – 0.4, malic – 0.3, oxalic – 0.05, coffee – 0.2. The moisture content of raw coffee is 9-12%.



Figure 2.3. Appearance of coffee grounds

Characteristics of chopped straw stalks. Straw (Figure 2.4) is agricultural waste from the stalks of grain plants. It is formed when grain is threshed together with other waste.

The chemical composition of straw depends on the type of plant, climate, method of harvesting, threshing, storage and other factors. Straw contains 35-45% fiber and other complex carbohydrates, 2-6% protein, 1.2-2% fat, 4-7% ash.



Figure 2.4. Appearance of chopped straw

2.2. Research methods

Biocomposite samples were obtained by hot pressing of a composition. The composition is formed based on a solution of gluten and natural fillers. The forming pressure was 10 MPa. Compressive strength was determined according to ASTM D695 "Compression testing of rigid plastics". Biocomposite samples are aged in a chamber of a drying oven or a refrigeration unit. The samples were compressed at a speed of movement of the traverse of the press of 2 mm/min.

The compressive strength limit is calculated by the formula:

$$\sigma = \frac{P}{S},$$

P – the maximum load before failure, N;

S – the cross-sectional area of the sample, cm².

Impact strength is determined by the Charpy method GOST 9454-78. The method based on a test in which a sample lying on two supports hit by a pendulum. The impact line is in the middle between the supports and directly opposite the notch in the case of specimens with a notch. The dimensions of the studied sample are 10×10×60 mm.

The impact strength is calculated by the formula:

$$KC = \frac{Q \cdot l \left[(\cos \beta - \cos \alpha) - (\cos \gamma - \cos \alpha) \frac{\alpha + \beta}{\alpha + \gamma} \right]}{S},$$

Q – weight of hammers of pendulum copra, kg;

l – distance from the axis of rotation to the center of weight of the hammer, m;

α – angle of rise of the pendulum, degrees;

β – angle of deflection of the pendulum after impact, degree;

γ – idle angle, degree;

S – cross-sectional area m².

Determination of hardness by the Brinell method was realized on the end surface of cylindrical samples, as a result of pressing a ball with a diameter of 5 mm with a force of 1875 N (Figure 2.5, a).

The resulting impression does not have sharp edge contrast for diameter measurements. Therefore, dye (chromium oxide) is applied to the surface (Figure 2.5, b). The imprint is obtained by pressing the indenter (Figure 2.5, c) with subsequent cleaning of the surface from the dye (Figure 2.5, d). As a result, the contrast between the surface of the workpiece and the imprint obtained, which allows you to measure the diameter with the required accuracy.

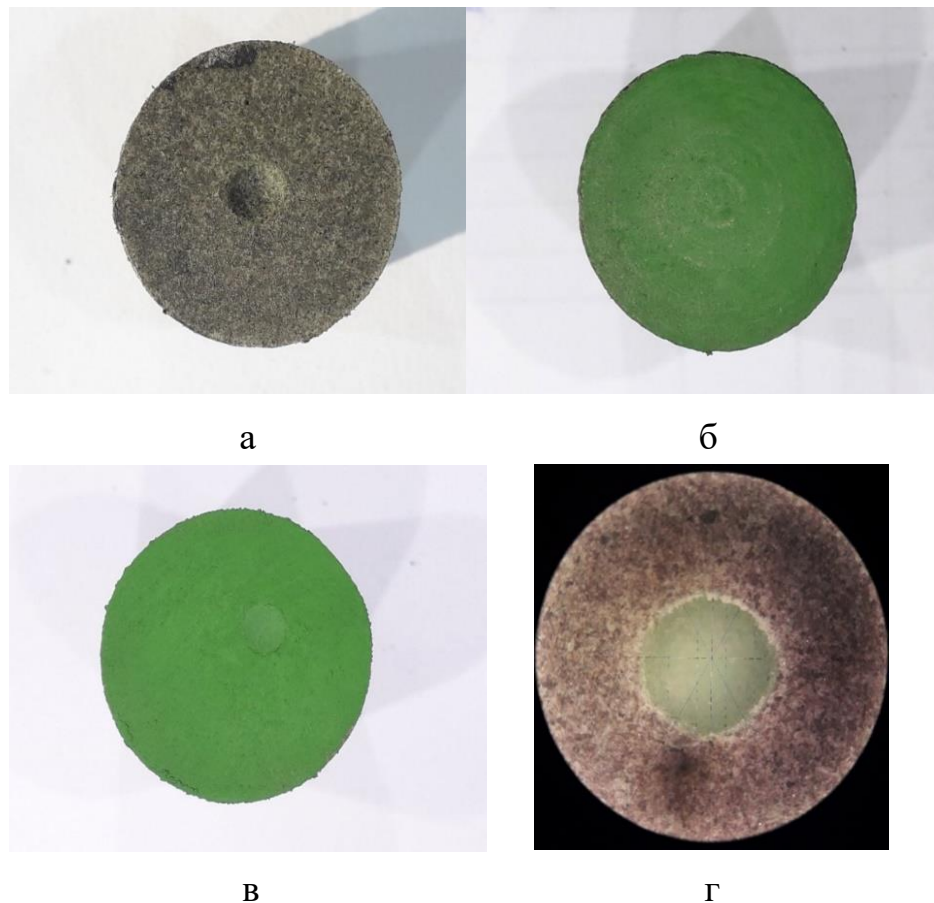


Figure 2.5. The surface of biocomposite sample: a – imprint of indenter on the end surface; б – end surface with dye; c – imprint of indenter on the end surface with dye; d – contrast of surface imprint and end surface

Brinell hardness (HB) is calculated by the formula:

$$HB = \frac{2P}{\pi D \left(D - \sqrt{D^2 - d^2} \right)},$$

P – applied load to the indenter, H;

D – ball diameter, mm;

d – diameter of the imprint, mm.

During operation, polymer products are exposed to temperatures (increased or decreased) depending on the environmental conditions. Therefore, determining the influence of this factor on the mechanical properties of polymer materials is an important process. Changing the properties of the material under the influence of temperatures

under normal conditions takes a long time, therefore, to accelerate the process of thermal aging in laboratories, artificial conditions of temperature exposure are created.

The degree of aging is assessed by the aging coefficient, which shows the level of reduction in material properties. For these studies, the samples have the form of bars (three samples for each temperature). Samples kept at temperatures lower than the operating temperature. After temperature aging, the material samples are tested for compressive strength. The obtained results are compared with the corresponding indicators of untreated samples and the aging coefficient K_{τ} is calculated according to the formula:

$$K_{\tau} = A_1 / A_0$$

A_0, A_1 – indicators characterizing the quality of the studied characteristic before aging and after it, respectively.

The result is the arithmetic mean value of at least three parallel measurements for indicators that differ by no more than 5%.

2.3. Formation technology of biocomposite samples

Bone glue was used as a binder to form a matrix of biocomposites filled with waste of natural origin. Wood flour, coffee grounds and shopped straw were used to fill the system. The content of fillers in the biocomposite material ranged from 80 to 130 mass parts.

Stages of formation technology of biocomposite. First, the ingredients are dried to remove moisture. The components of the material are dosed on analytical balances VLA-200 with an accuracy of 0.0001 g.

The formation of test samples consists in mixing an aqueous solution of gluten and filler. Gluten is dissolved in water for 3 hours at a temperature of 50 °C with the calculated ratio of components.

The content of gluten granules (m) is calculated by the formula:

$$m = \frac{x \cdot m_p}{100 - W},$$

x – concentration of the solution, %

m_p – mass of the solution, g;

W – moisture content of gluten granules, %.

Water content (m_w) is calculated:

$$m_w = m_p - m$$

The samples were formed in a press form consisting of a bushing and punches that compress the composition inside the bushing. Forming and heat treatment of biocomposites implement under pressure. Heating to 40 °C for 1 hour leads to shrinkage due to a decrease in the viscosity of the composition and removal of water. Heating to 60 °C for 2 hours leads to shrinkage due to intensive removal of water. After 1.5 hours at a temperature of 80 °C, the structuring of the gel begins, while the composition remains unstructured. Exposure for 1.5 hours at 130 °C provides solidification of the biocomposite. Shrinkage is from 5 mm to 9 mm along the height of the sample.

To avoid elastic aftereffect and expansion of the material during heat treatment, the punches are fixed with a clamp, which additionally compresses the composition in the mold. After heat treatment of the composition, the sample is removed from the press form. Next, the samples are subjected to additional heat treatment.

CHAPTER 3

BIOCOMPOSITES FILLED WITH WOOD FLOUR

3.1. Development of forming technology of biocomposite products filled with wood flour

The formation of biocomposite products based on a glutin solution, into which a filler (wood flour) was introduced, requires the development of a technology that includes the following operations: preparation of components, dosage, preparation of the composition, preparation of the mould, loading of the composition, pressing, heat treatment, removal of the product, drying.

The preparation of the filler consisted in drying the wood flour at a temperature of 110 °C for 2 hours and sifting the particles through a sieve with a hole size of 0.2-0.3 mm. As a matrix, a 40% solution of glutin was used, which was obtained by dissolving bone glue granules in a dosed amount of cold water in a hermetic vessel and keeping the water-saturated granules in a drying cabinet for 2 hours at a temperature of 50 °C. In the case of the dissolution of granules in hot water (70-80 °C), the glutin saturation process occurred more intensively, because hydrogen bonds between amino acid macromolecules were destroyed under the influence of elevated temperature.

The duration of the preparation of the glutin solution was reduced to 30 minutes, which is a positive point in the development of the technological process, but as a result of the use of such a solution, the product after removal from the mould remains plastic and does not completely transition into a solid state. This leads to the destruction of the product during removal from the mould with the formation of cracks or delamination (Figure 3.1), the appearance of which is due to insufficient structuring of the biopolymer matrix.

At the final stage of formation, the resulting solution is mixed to equalize the density due to the formation of a homogeneous distribution of amino acid macromolecules in the medium of the water solvent. The solution is prepared immediately before introduction into the wood flour since during the cooling process a

gel-like structure is formed, which is not suitable for combining with finely dispersed filler.

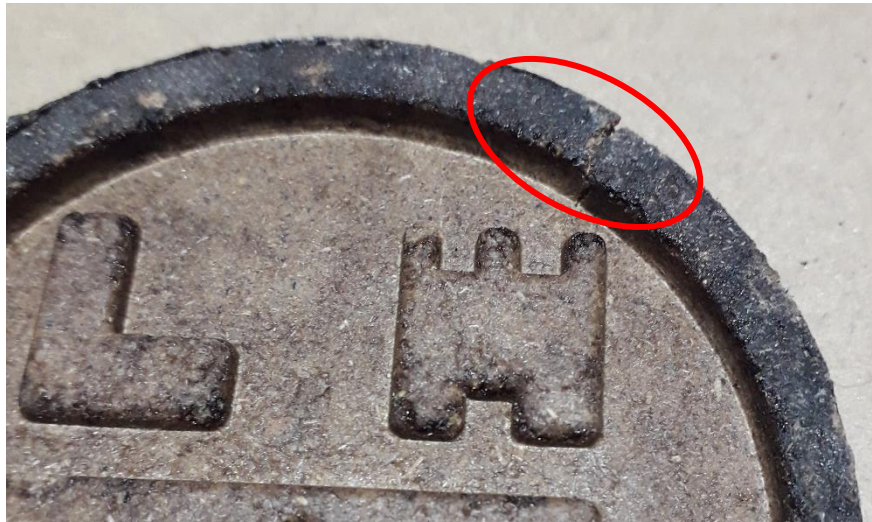


Figure 3.1. View of a part of a decorative product with a crack on the contour protrusion

It was experimentally determined that the optimal content of wood flour is 100 mass parts per 100 mass parts glutin solution, which ensures the formation of a biocomposite material with high compressive strength values (20-25 MPa). In the case of using a higher content of filler, the particles of wood flour are not completely wetted by the solution. In the case of using a lower content of the filler, the intensive release of the binder occurs during the main heat treatment through the gaps of the mould, as a result of which there is a significant loss of the biopolymer matrix, which ultimately leads to a decrease in the mechanical characteristics of biocomposites.

Preparation of the composition consists in combining a liquid glutin solution with a dosed amount of wood flour, followed by mixing the mixture until the particles are completely saturated with the solution within 2-3 minutes and obtaining a homogeneous composition. After homogenization, the composition is dosed, which is subjected to preliminary heat treatment by drying to establish the optimal moisture content in it (12%).

In the case of excess moisture removal, 15-20% of gluten macromolecules lose their ability to transition into a liquid state and interact with wood flour particles. As a result, there is an uneven distribution of the biopolymer binder in the volume of the product, which leads to the peeling of the particles. This happens due to the direct contact of wood flour particles with each other without the presence of a layer of biopolymer matrix, which leads to the destruction of the biocomposite material in the form of fragmentation of filler particles (Figure 2, a). In case of insufficient removal of moisture (8-10%), the binder is removed through the cracks of the mould during the main heat treatment, as a result of which a part of the biopolymer matrix is lost and fogging is formed at the edges of the product (Figure 3.2, b).



Figure 3.2. Appearance of the product with defects: a – the area of cracking;
b - the area of the storm

The operation of preparing the mould consists in preparing the working surfaces for contact with the composition by lubricating with a special lubricant (50% paraffin + 50% oil) to avoid adhesive bonding of the biopolymer matrix with the surface of the mould. If the amount of lubricant is insufficient, local adhesion occurs, with the formation of an inseparable connection of the biocomposite product with the surface of the mould walls. This complicates the process of removing the product, as a result of which the surface layer (Figure 3, a) of the biocomposite material is destroyed, which reduces the quality of the decorative appearance of the product and causes an additional

puttying operation. In the presence of an excess layer of lubricant during heat treatment, the surface of the biocomposite material is saturated with lubricant components, as a result of which the surface acquires lyophobic properties (Figure 3.3, b). This complicates the process of applying a protective coating, as macromolecules of the colouring material are repelled from the surface of the product, which is saturated with a layer of lubricant.



Figure 3.3. Appearance of the product with defects: a – delamination zone;
b – lyophobic surface of the biocomposite product

The working surface of the mould should have an optimal roughness ($R_a=1.2$) to avoid adhesive bonding of the biopolymer matrix with the side surface of the matrix and the end surface of the punches after thermo-mechanical processing. Low adhesive strength will ensure the convenient removal of the product from the mould matrix and separation from the flat surfaces of the punches without forming craters.

The prepared composition is poured into the cavity of the matrix, closed with the upper punch and pressed under a pressure of 12 MPa, followed by holding for 60 seconds to equalize the specific load on the walls of the mould. To avoid moving the punches during heat treatment, they are fixed. Further, the mould is placed in a drying chamber with a temperature of 120 °C for 1 hour. In the case of an insufficient heat treatment temperature (100 °C), the biocomposite material remains plastic, which leads

to the removal of residual moisture and the formation of layers during the next additional heat treatment of the product (Figure 4, a). If the heat treatment temperature is higher than the optimal one (140 °C), the destruction of the biopolymer matrix occurs in the locations of protrusions with sharp corners or sharp changes in relief, where the concentration of thermal energy occurs (Figure 3.4, b).

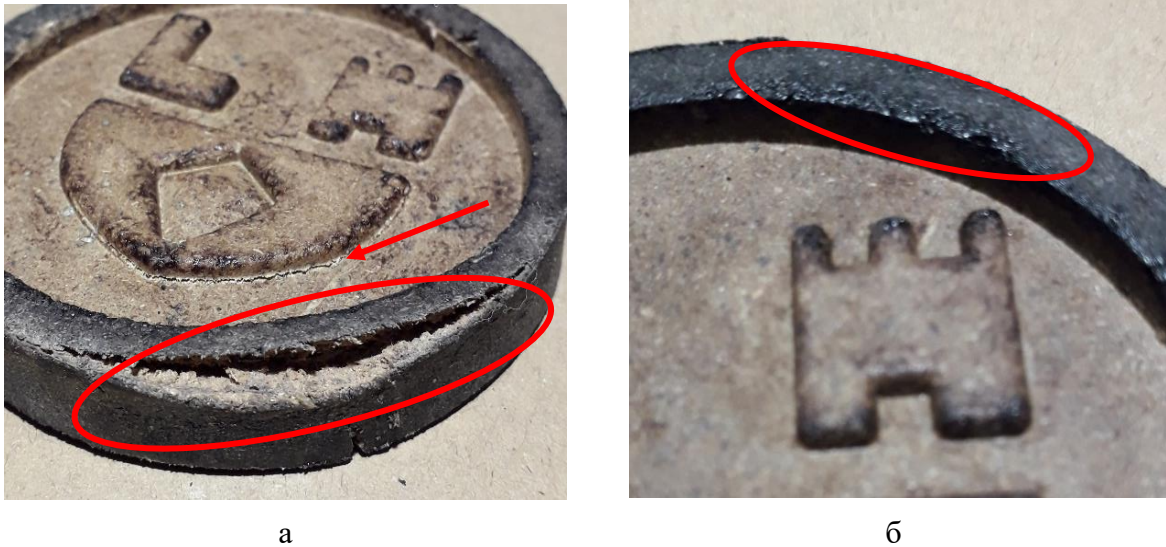


Figure 3.4. Appearance of the product with defects: a – delamination zone;
b – the destruction zone of the biopolymer matrix

Processing of biocomposite material in a thermal field leads to the intensive release of moisture, as a result of which voids are formed inside the product, which significantly reduces the mechanical characteristics of the biocomposite material. The application of additional compression during the main heat treatment ensures the restoration of the integrity of the biopolymer matrix due to the approximation of amino acid macromolecules and the formation of physicochemical bonds.

After completion of thermo-mechanical treatment, the mould is removed from the chamber of the drying cabinet and cooled to room temperature. When the heated product is removed from the matrix, individual elements are destroyed (Figure 3.5) as a result of the low heat resistance of the biopolymer matrix and the presence of the biopolymer in a liquid or highly elastic state, which does not ensure the high strength of the biocomposite material.

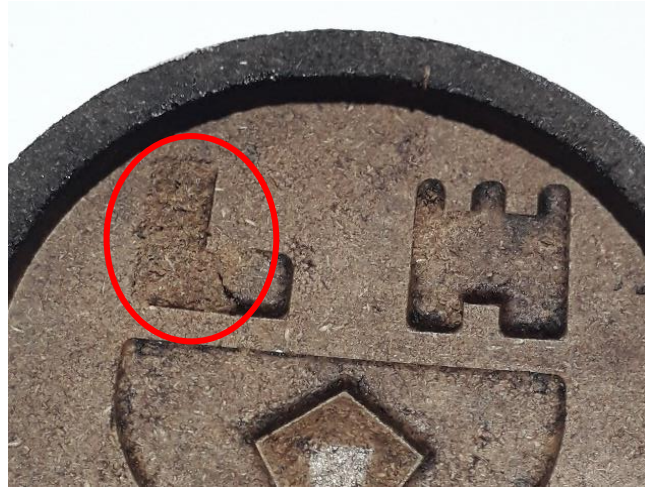


Figure 3.5. Defective appearance of the product with an area of destruction of the protruding element

At the final stage, the products are subjected to additional heat treatment at a temperature of 50 °C for 1 hour to remove residual moisture and reduce the degree of stress that occurs in the biocomposite material during thermomechanical processing. If all technological factors are taken into account and the biocomposite formation process is carried out under optimal conditions, we will get a product without structural defects with a satisfactory decorative appearance and high mechanical characteristics (Figure 3.6).



Figure 3.6. The general appearance of the decorative product without structural defects

Conclusions. The formation of biocomposite products based on the glutinous matrix requires the development of a special technology, which consists of the combined processing of the composition under the influence of thermal and mechanical fields. The thermal field ensures the transfer of the glutinous solution from a gel-like state to a liquid state, as a result of which the surface of wood flour particles is wetted with a binder and new physico-chemical bonds are formed. The compressive force brings the macromolecules of amino acids closer together, the separation of which occurs as a result of the removal of water molecules during the main heat treatment. The approach of macromolecules contributes to the restoration of the integrity of the biopolymer matrix and the formation of additional physical and chemical bonds. Carrying out additional heat treatment ensured a decrease in the tension of the surface layers, which are in a more compressed state compared to the central area, as well as the removal of water residues, which reduces mechanical characteristics. As a result of experimental studies, the modes of formation of biocomposite products at the stage of preparation, formation and additional processing of the composition were optimized, which made it possible to obtain a decorative product with high strength (20-25 MPa) and resistance to wear of the surface layer.

3.2. Operational properties of biocomposites filled with wood flour

It was experimentally established that biocomposite samples exposed to a temperature of 70 °C for 96 hours have the lowest compressive strength (20 MPa), which is explained by the presence of high internal stresses in the system (Figure. 3.7). Up to a temperature of 50 °C, the compressive strength limit decreases gradually by 20-30%, and with the subsequent increase in temperature, this characteristic decreases sharply.

It was experimentally established that the maximum compressive strength values (57.1 MPa) have biocomposite samples exposed to a minimum temperature of 40 °C and a minimum holding time of 0.5 h.

At a holding temperature of 40 °C, the compressive strength limit is 60-70% of its value at room temperature. The mechanical properties of materials depend on the duration of the test. At some temperatures, the tested sample can be destroyed under a lower degree of stress than at room temperature, if the structural elements of the biocomposite material will perceive stress for a long enough period.

The strength limit when compressing materials at high temperatures is not characterized by the value of the usual strength limit, which is determined by short-term tests, but by the value of the so-called long-term strength limit.

The effect of temperature on the change of various properties can be easily measured by the nature of these changes, which consists mainly of the effect of temperature on the flexibility of macromolecules. The question of the effect of temperature is complicated if the material decomposes during heating. The most important reactions that occur during decomposition are destruction and structuring, these reactions have the opposite effect on the properties of the polymer. Thus, during ageing in air, as a result of the destruction, softening of the material occurs, while structuring leads to the formation of a brittle product.

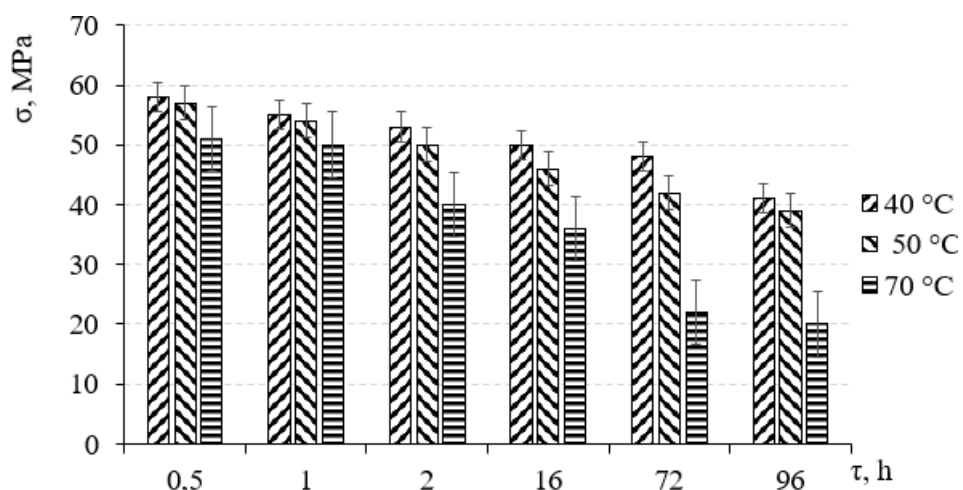


Figure 3.7. Dependence of the compressive strength of biocomposites on the heating temperature and duration of exposure in the thermal field

With long exposure of the polymer at a constant temperature or with a gradual increase in temperature, its strength may first decrease due to the destruction of chains

and then increase again due to structuring. Eventually, the strength decreases again as a result of the complete decomposition of the polymer. Continuous long-term high-temperature pyrolysis can cause carbonization, which usually leads to an increase in dielectric losses and a decrease in electrical strength [69].

Analysis of experimental results (Figure 3.8) shows that during compression, a sharp drop in this characteristic occurs at temperatures above the limits of heat resistance. Depending on the type of influence of the physical field (increased or reduced temperature, cyclic temperature change) and the chemical structure of the polymer, a significant change in physical and mechanical characteristics may occur. At the same time, the characteristics can increase or decrease significantly, which can be explained by the fact that its heat resistance decreases, thermal destruction is facilitated and the output of flammable gaseous products increases. The influence of temperature on polymers is determined, first, by the behaviour of the matrix. It is known that in the region of the glassy state, with increasing temperature, the deformation-strength properties of polymers slowly decrease until reaching the limit of heat resistance, exceeding which is accompanied by an accelerated decrease in characteristics. In some cases, in the temperature range.

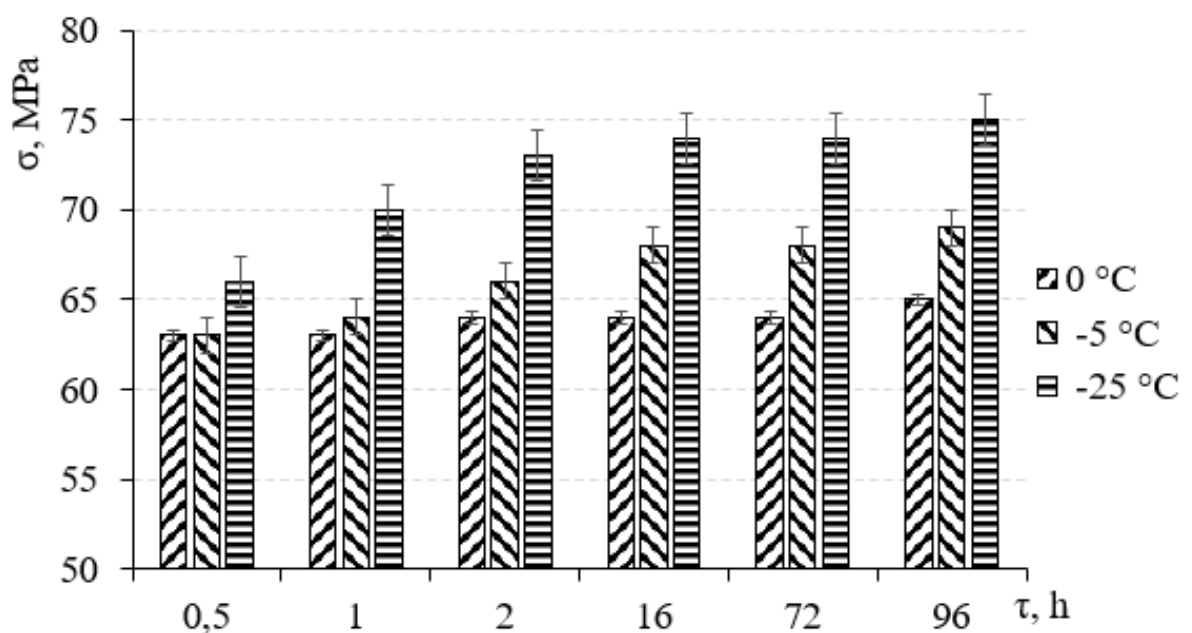


Figure 3.8. Dependence of the compressive strength of biocomposites on the cooling temperature and duration of exposure at low temperatures

At 10-20 °C, the value of the modulus of elasticity and destructive stress decreases by two decimal orders. The presence of dispersed fillers, which have an additive effect on the composite, somewhat smooths his intensity of reduction, and in the case of highly filled systems, the transition of the polymer from a solid, glassy to a highly elastic state occurs even more slowly [70].

The limit of the strength of biocomposites at the test temperature of 0 °C is 63-65 MPa, while the duration of exposure has little effect on this characteristic. Cooling to a temperature of -5 °C provides an increase in the strength limit under compression by 5-13%, which is associated with a change in the parameters of the structural elements of the biopolymer matrix as a result of a decrease in the mobility of amino acid segments under conditions of cooling of the biocomposite. With an increase in the duration of exposure of biocomposites to 96 hours, there is a further increase in the resistance of the material to static loads at a temperature of -25 °C, which is due to the appearance of crystalline water inclusions in the recesses of the glutinous biopolymer network, as well as a decrease in the plasticity of the biopolymer matrix.

It was experimentally established that the process of destruction of biocomposite samples occurs unevenly, which is related to the peculiarities of the formation of the structure of the biopolymer matrix and depends on the chemical composition and temperature of the environment in which the biocomposite samples are located. Biocomposite samples placed in hot water at a temperature of 70-80 °C have a high rate of destruction. At the same time, the duration of degradation is 20 minutes. This is due to the dissolution of the biopolymer matrix, as a result of which gluten macromolecules and organic filler particles pass into the aqueous medium. It was recorded that biocomposite samples that are completely immersed in hot water degrade the fastest compared to other environments. Degradation of biocomposite samples in the environment of HCl solution completely occurs after 42 minutes, because under the action of chemical agents, the crystalline macromolecular structure is destroyed, which in some cases leads to the formation of monomers. As a result, the process of destruction of the biopolymer matrix occurs, which leads to the separation of the filler particles and the delamination of the material [71].

The duration of the destruction of biocomposite samples in cold water is 120 minutes. It was experimentally established that biocomposite samples that are partially immersed in cold water in a desiccator degrade more slowly compared to samples that are completely immersed in cold water. This means that the glutinous matrix slowly adsorbs moisture due to the high packing density of the components of the biocomposite material, which is formed under high pressure (10 MPa) and a heat treatment temperature of 150 °C. Partial destruction of biocomposite samples in a 10% NaCl solution occurs during 650-700 minutes. As a result of experimental studies, it was established that biocomposite samples that are completely immersed in a 10% NaCl solution are almost indestructible compared to samples that are immersed in cold water or hot water. The degradation mechanism of biocomposite samples is determined by the degree of water absorption, which leads to the dissolution of the glutinous matrix, however, in the case of using a sodium chloride solution, the intensity of absorption slows down due to the selective sorption of water molecules, sodium cations, and chlorine anions.

Conclusions. It was established that the compressive strength of glutinous biocomposite materials filled with wood flour powder decreases when the ambient temperature rises, which is due to the low heat resistance of the biopolymer matrix. The segments of gluten macromolecules increase their mobility as a result of heating, and the bonds between the nonpolar groups of the chain sections of gluten macromolecules are destroyed, which contributes to the plastic deformation of the biocomposite material. Therefore, it is advisable to use products based on glutinous biocomposites in conditions of low temperatures, which ensures an increase in the compressive strength limit by 65-75% compared to the operating temperature of 50-70 °C.

The developed biocomposite materials are resistant to moisture and sodium chloride solution for quite a long time, which is due to the high density of structural elements of biocomposites. This allows the use of biocomposite products in conditions of short-term exposure to moisture without delamination and destruction of the biopolymer matrix.

In the future, it is planned to treat the surface of the products with antiseptic agents and to investigate the effect of protective paint coatings on resistance to the effects of atmospheric factors in order to increase the duration of operation in difficult conditions of exposure to chemical aggressive substances and cyclic temperature changes.

CHAPTER 4

OPTIMIZING THE FORMING TECHNOLOGY OF BIOCOMPOSITES FILLED WITH CHOPPED CEREAL STALKS

Biocomposite samples based on gluten were formed. Biocomposites contain 130, 140 and 150 mass parts of chopped cereal stalks fractions 0.5 and 0.7. Samples were formed by pressing the composition. Thermal treatment of biocomposites (TO_1): exposure for 2 hours at a temperature of 150 °C (after 1 hour, the composition must be pressed). Then, the samples in the press form are removed from the drying oven and are cooled at room temperature. After cooling, the biocomposite samples were removed from the press form. Then, for biocomposites (Figure 4.1), additional heat treatment TO_2 (drying) is performed. Mode of additional heat treatment TO_2 : holding for 1 hour at a temperature of 80 °C, 1 hour at 100 °C, 1 hour at 150 °C.



Figure 4.1. Appearance of biocomposite samples filled with chopped cereal stalks

During compression, biocomposite samples obtain a barrel shape (Figure 4.2) because of their delamination or plastic deformation. This indicates insufficient structuring (solidification) of the biocomposite due to the presence of excess moisture in the biocomposite materials, which not completely removed during heat treatment.

To increase the strength of biocomposites after heat treatment (TO_1), the samples were removed from the press form and left for 7 days at room temperature for additional

moisture removal from the composition. Biocomposite materials (Table 4.1) containing 140 mass parts chopped cereal stalks of fraction 0.7 were formed.



a

b

Figure 4.2. The appearance of biocomposite samples filled with chopped cereal stalks after compression: a – 140 mass parts, fraction 0.5; b – 150 mass parts, fraction 0.7, ×2

Table 4.1.

Heat treatment modes of biocomposites

Sample No	TO ₁ (2 h 150 °C)	Exposure time 8 h, 50 °C / day	TO ₂ (1 h t=80 °C, 1 h t=100 °C, 1 h t=150 °C)	Exposure, day	Exposure 8 h, 50 °C
1	+	+/-	+	-	-
2	+	+/-	+	7	-
3	+	+/-	+	4	+
4	+	+/-	+	7	+
5	+	-/7	+	2	-

The next stage of the technological process is additional thermal treatment TO_2 (drying) for biocomposites: 1 hour at 80 °C, 1 hour at 100 °C, 1 hour at 150 °C. After each exposure, we weigh the samples and determine the mass loss of biocomposite materials. To optimize the technology of obtaining biocomposites, it is proposed to dry the samples at a temperature of 50 °C for 8 hours after TO_1 heat treatment.

The highest compressive strength of 53.3 MPa (Figure 4.3) has biocomposites formed according to mode No. 2. This is ensured by the formation of a homogeneous structure without macrocracks (Figure 4.4) due to the uniform gradual removal of residual moisture in the material during additional heat treatment. The biocomposite strengthens also because of its aging for 7 days (under normal conditions) due to the additional removal of excess moisture from the volume of the material.

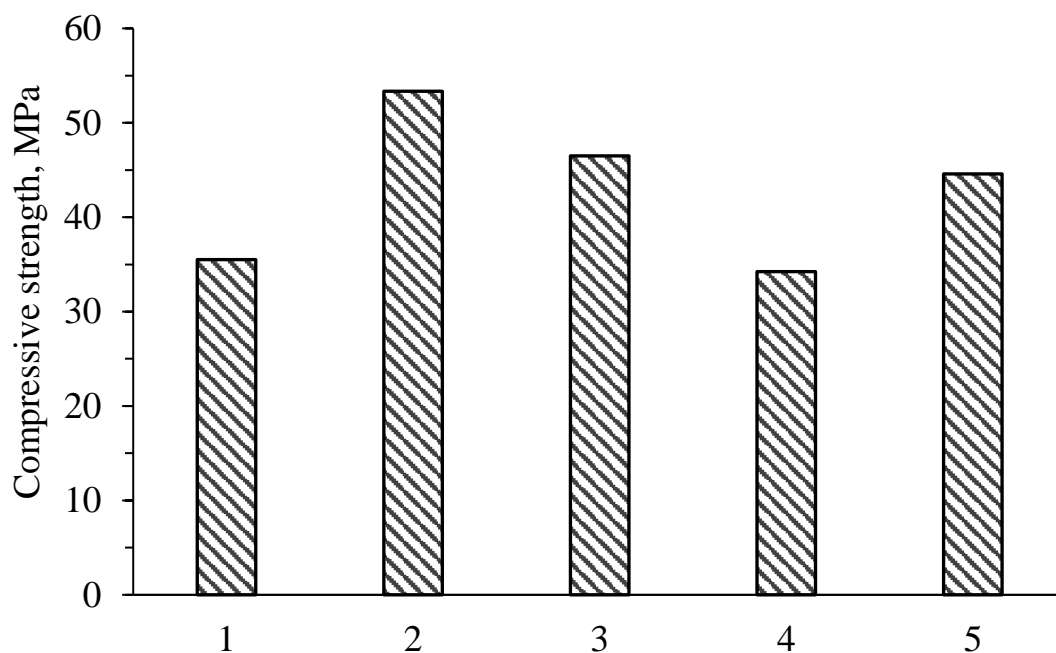


Figure 4.3. Compressive strengths of biocomposites formed according to the regimes in the table 4.1

The biocomposite sample formed according to technology No. 3 has a lower compressive strength (46.5 MPa) by 13%. This sample has a shorter exposure to air (4 days). This indicates the importance of slow additional removal of excess moisture from the biocomposite material at the last stage of its structuring (after the main (TO_1))

and additional (TO_2) heat treatment of the composition). This can be effected by lowering the temperature and increasing the exposure time.



Figure 4.4. The appearance of a biocomposite sample ($\times 2$)
formed by technology No. 2 (Table 4.1)

Biocomposites formed according to mode No. 5 have a 4% lower compressive strength (44.6 MPa) compared to the previous sample. In the technology of obtaining this biocomposite material, after the main heat treatment of the composition (TO_1) and before the additional heat treatment of the composite (TO_2), the sample is left under normal conditions for 7 days. At this stage of biocomposite structuring, higher temperatures are necessary to ensure the increase in structural strength of the material. For biocomposites formed according to regimes No. 2 and No. 3 the samples were dried at a temperature of 50 °C for 8 hours (instead of holding for 7 days under normal conditions).

Biocomposites formed according to mode No. 4 have the lowest compressive strength of 34.2 MPa. In order to remove excess moisture additionally (compared to mode No. 2), the samples were dried at a temperature of 50 °C for 8 hours. During drying, moisture was quickly removed from the material, which led to the destruction of the physical and chemical bonds between the components of the biocomposite.

Microcracks are formed in biocomposites. Cracks are stress concentrators and contribute to the destruction of the material under the action of static load.

Biocomposites formed according to mode No. 1 have a higher (by 7%) compressive strength of 36.6 MPa. This biocomposite sample did not dried after additional heat treatment. Therefore, the biocomposite not sufficiently structured due to excessive moisture content in the material

The formation of a more uniform structure (Figure 4.5) is observed for the biocomposite formed by mode No. 2 compared to the biocomposite formed by mode No. 4. The biocomposite sample formed by mode No. 2 has fewer pores with a smaller diameter.



a



b

Figure 4.5. The appearance of the fracture surface of biocomposites formed according to modes No. 2 (a) and No. 4 (b)

To optimize the forming technology, before forming the samples in the press form, a drying stage of the composition (preliminary heat treatment) was introduced. Preliminary heat treatment of the composition at temperatures of 60-80 °C is performed to reduce the moisture content by 10%, 15%, 20% and 25%. To form a biocomposite sample with a height of 30 mm and a diameter of 20 mm, 11 g [23] of the dried composition is needed, which ensures the optimal density of the biocomposite material. After that, the dried composition is placed in a press form and pressed under a specific load of 10-15 MPa. The punches are fixed with clamps to avoid expansion of the composition because of the elastic aftereffect and the action of water vapor during the main heat treatment (TO₁) according to the established regime (Table 1). After heat treatment (TO₁), the biocomposite is pressed out of the press form and subjected to additional heat treatment in a drying cabinet according to the TO₂ mode (Table 4.2).

Table 4.2.

Forming modes of biocomposites

Mode No	TO ₁	TO ₂
1	TO (t = 150 °C, τ = 1 h) + additional compression + TO (t = 150 °C, τ = 1 h)	—
2		t = 50 °C, τ = 4 h
3		t = 80 °C, τ = 4 h
4		t = 100 °C, τ = 4 h

The lowest compressive strength of 7.9 MPa and 7.2 MPa has biocomposites (Figure 4.6) filled with chopped cereal stalks with a particle fraction of 0.5 mm and 0.7 mm, respectively. These biocomposites have a high moisture content, as the loss of moisture during the preliminary heat treatment was 10%. This can be explained by the excessive content of moisture in the material, which prevents the complete structuring of biocomposites. Water molecules are intensively removed during the main TO₁ heat treatment of the composition in the press form, that lead to delamination of the biopolymer matrix in the form of voids and cavities, which significantly reduces the strength of biocomposites. Reducing the moisture content of the composition to 15%

led to a 4.4-4.7 times increase in the compressive strength of biocomposites, which is 38.2 MPa and 31.8 MPa for samples filled with chopped cereal stalks in fractions of 0.5 mm and 0.7 mm respectively. The increase in strength of biocomposites is due to the formation of a more rigid structure of the biopolymer matrix because of the removal of excess water content.

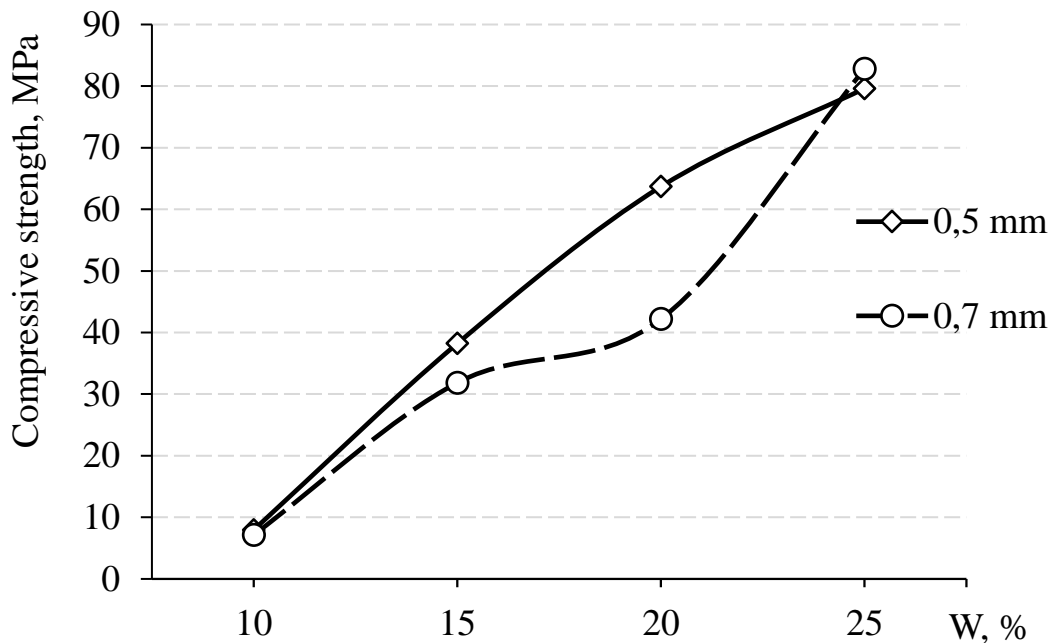


Figure 4.6. Dependence of the compressive strength of biocomposites filled with crushed cereal stems (0.5 mm and 0.7 mm fraction) on the decrease in the moisture content of the composition during preliminary heat treatment

The compressive strength of biocomposites with a drying degree of 20% increases by 1.3-1.7 times compared to biocomposites whose compositions lost 15% of moisture. The residual moisture content is sufficient to convert gluten during heat treatment into a gel-like state, which contributes to the formation of a homogeneous structure of the biopolymer matrix. Macromolecules of heated gluten are adsorbed on the surface of cereal stalk particles and form additional physicochemical bonds because of removing residual moisture. Biocomposites filled with cereal stalk particles with a size fraction of 0.5 mm have 35-40% higher compressive strength values (63.7 MPa) compared to the compressive strength values (42.2 MPa) of biocomposites containing cereal stalk particles with with a fraction size of 0.7 mm. The higher compressive strength of

biocomposites is due to the formation of more homogeneous composite containing particles of cereal stems 0.5 mm long. Smaller particles contribute to the formation of a structure with a higher degree of compaction due to their compact arrangement. In addition, the fibers of the stems have a fibrillar structure in the form of a collection of capillary fibers. During heat treatment, gluten changes into a liquid state, which allows the solution to enter the fibrils and fill them. If short fibers (0.5 mm) are used, a larger volume of gluten solution fills the fiber cavity compared to fibers with a length of 0.7 mm. For longer fibers, the gluten solution fills a much smaller volume of the fiber cavity. Therefore, biocomposites have lower strength due to the presence of a larger volume of cavities. For biocomposites with a lower moisture loss (10% and 15%), this effect is not very noticeable, since excess moisture ensures a higher fluidity of the gluten solution. As a result, gluten macromolecules are able to fill a higher volume of cavities of fibrils of crushed cereal fibers.

Biocomposites with a higher drying degree of composition (moisture loss of 25%) have a 50% higher compressive strength for composites with a fraction of 0.7 and by 22% for composites with a fraction of 0.5. This can be explained by the absence of macroscopic defects in the structure, which arise because of a decrease in moisture.

Biocomposite materials with a drying degree of 10% have a uniform distribution of filler particles in the volume of the biopolymer matrix (Figure 4.7, a). On the surface of the biocomposite material with a drying degree of the composition up to 15%, the inclusion of particles of stalks, which have a light color, was recorded. This indicates a reduced content of the glutinous matrix in the interparticle space (Figure 4.7, b). On the surface of the biocomposite material with a drying degree of the composition of 20%, randomly arranged stalk particles are observed, which contain a minimal amount of gluten matrix macromolecules on the surface (Figure 4.7, c).

In order to increase the rigidity of the glutinous matrix of biocomposites, additional thermal treatment of TO_2 is performed at different temperatures (50 °C, 80 °C and 100 °C) with exposure for 4 hours, which remove the residual water content (Table 4.1, processing modes No. 2, 3, 4). The composition is dried to a moisture loss

of 10%, 15%, and 20%. Degree drying of 25% is not used due to the long-term process of removing water and the loss of manufacturability of the composition, when it is necessary to apply high compressive forces, which leads to the appearance of an elastic aftereffect and the appearance of a stressed state.

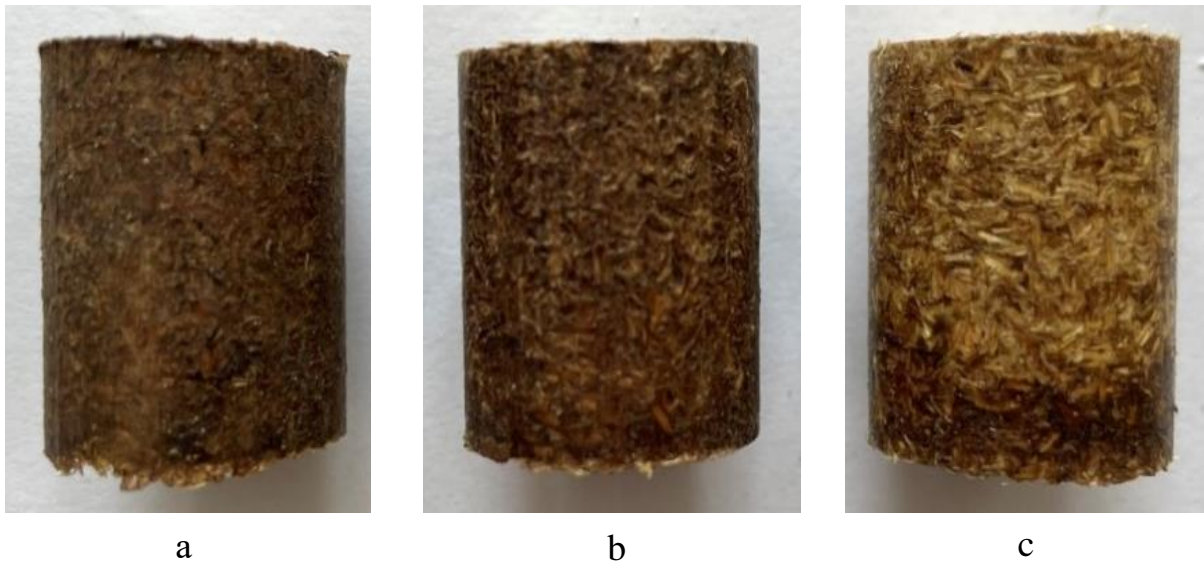


Figure 4.7. The appearance of biocomposite samples with the preliminary drying degree of the composition: a – 10%; b – 15%; in - 20%

The compressive strength of biocomposites with a drying degree of the composition of 10% and additional heat treatment of the finished products at a temperature of 50 °C for 4 hours is 33.4 MPa (Figure. 4.8). Biocomposites with a drying degree of composition of 15% have a higher compressive strength of up to 45.3 MPa. This is due to the removal of water residues from the volume of the biocomposite material, which contributes to the formation of a dense structure without defects. Increasing drying degree of the composition to 20% allows obtaining biocomposites with a compressive strength of 87.6 MPa. This is due to the slow removal of minor residues of water molecules and the formation of the maximum number of physicochemical bonds between the biopolymer matrix and the surface of the filler particles.

Additional heat treatment at a temperature of 80 °C for 4 hours provides a 35% increase in compressive strength of biocomposites with a drying degree of 10%

compared to biocomposites with additional heat treatment at a temperature of 50 °C. The higher temperature of the additional heat treatment of 80 °C provides a significant removal of moisture, since the loss of water in the composition during the preliminary heat treatment was only 10%. The formation of biocomposites with a drying degree of 15% does not lead to an increase in compressive strength. The use of compositions with a moisture loss of 20% ensures a 35% increase in the compressive strength of biocomposites. This is due to the formation of additional physico-chemical bonds because of densification of the biopolymer matrix. The biocomposite system maximally reduces the moisture under this mode of additional heat treatment.

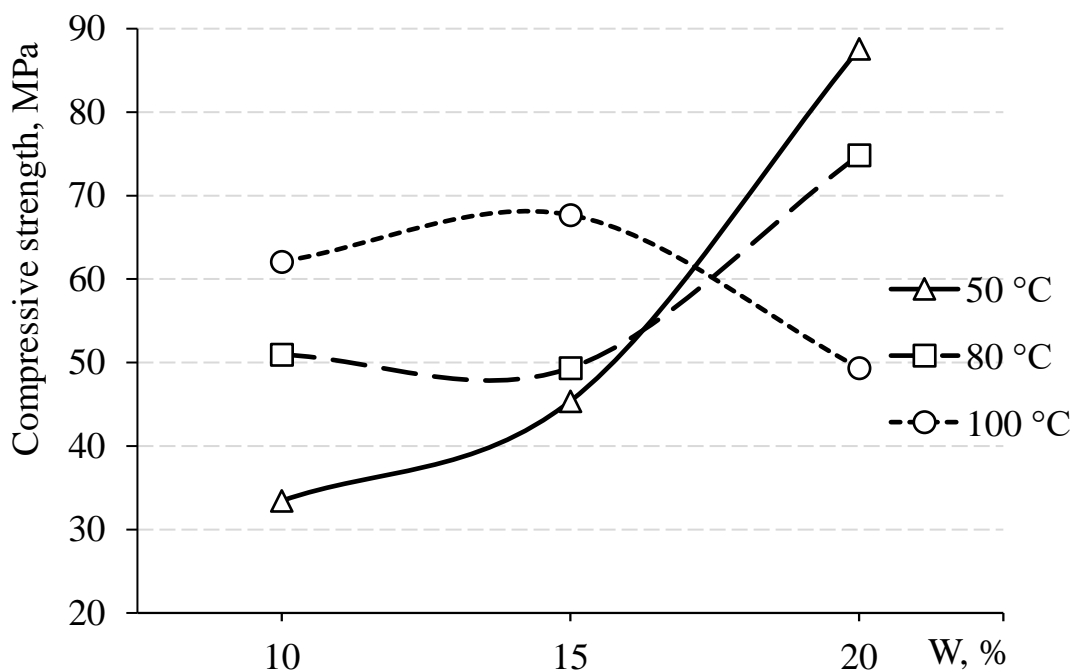


Figure 4.8. The dependence of the compressive strength of biocomposites filled with crushed cereal stalks (0.5 mm fraction) on the decrease in moisture content of the composition during preliminary heat treatment and exposure in a heat field for 4 hours during additional heat treatment

Biocomposites with a drying degree of composition of 15% and an additional heat treatment temperature of 100 °C have the maximum compressive strength. When the drying degree is increased to 20%, the compressive strength of biocomposites decreases, as the chains of gluten macromolecules are deformed and the elasticity of the biopolymer matrix is lost.

In order to improve the technological process, the duration of additional heat treatment of biocomposites filled with crushed stalks of cereals with a fraction size of 0.5 mm was reduced to 3 hours at elevated temperatures (100-120 °C) (Figure 4.9).

The lowest values of compressive strength (49.4 MPa) have biocomposites with a drying degree of composition of 10% at an additional heat treatment temperature of 100 °C for 3 hours. An increase in the compressive strength to 60.5 MPa occurs for biocomposites in case of an increase in the temperature of additional heat treatment to 120 °C. This is due to the removal of excess water content because of the action of thermal energy. The quantitative effect of thermal energy is determined by an increase in temperature (120 °C) or duration of exposure (4 h).

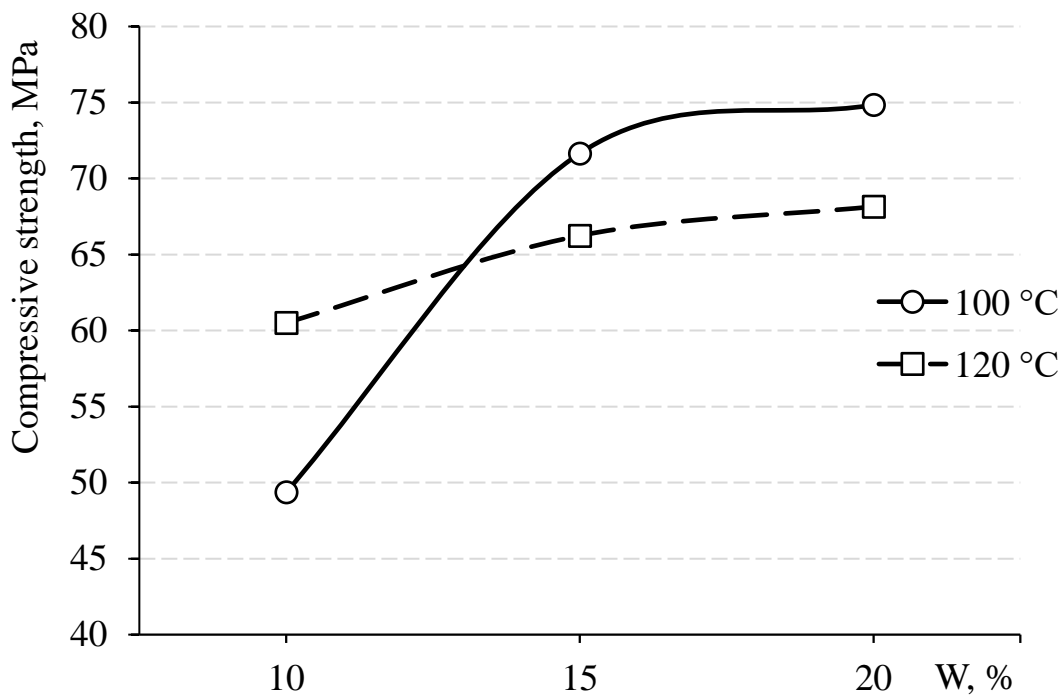


Figure 4.9. The dependence of the compressive strength of biocomposites filled with crushed cereal stalks (0.5 mm fraction) on the decrease in moisture content of the composition during preliminary heat treatment and exposure in a heat field for 3 hours during additional heat treatment

When the preliminary degree of drying of the composition is increased to 15%, the compressive strength of biocomposites additionally treated at a temperature of 100 °C for 3 hours increases by 1.1-1.5 times compared to biocomposites with a drying

degree of 10%. An increase in moisture loss to 20% does not provide a significant increase in compressive strength. Strength is determined by the ability of the biopolymer matrix to form the framework of a grid of gluten macromolecules with an optimal ratio of parameters of structural elements and to maintain the rigidity and elasticity of the framework of the biopolymer matrix under the influence of static loads.

The use of an additional heat treatment temperature of 120 °C leads to a 10% decrease in the compressive strength of biocomposites, the compositions of which dried during preliminary heat treatment until the moisture content decreased to 15% and 20%. This is due to the partial destruction of the physical and chemical bonds between the components of the biocomposite material.

Conclusions. Biocomposites with the composition dried to a loss of 25% moisture have the highest compressive strength compared to biocomposites whose compositions contained more moisture. At this drying degree, biocomposite materials with different fillings with a fractional composition (0.5 and 0.7 mm) have high compressive strength (79-83 MPa). This is explained by the transition of the biopolymer binder to a solid state with a minimal possibility of moving the chains of macromolecules of the gluten matrix. This is also explained by the absence of macroscopic defects in the structure, which can occur during heat treatment of the biocomposite material.

When the composition dried to 20%, there is a minimal amount of macromolecules of the gluten matrix on the surface of the particles of cereal stems. This ensures a high density of the biocomposite material.

Biocomposite materials with composition drying up to 20% after additional heat treatment at a temperature of 50 °C for 4 hours have high compressive strength (87.6 MPa) compared to biocomposites that were in a thermal field at temperatures of 80 °C and 100 °C. The remaining of water, that contained in the gluten solution, evaporates slowly under this mode of heat treatment. In this case, additional physicochemical bonds formed between the glutinous matrix and the surface of the cereal stem particles.

Biocomposites with a drying degree of composition of 15% and 20% have increased compressive strength by 30-35% compared to biocomposites with a drying degree of the composition of 10% in case of additional heat treatment at a temperature

of 100 °C for 3 hours. Under such a regime of stepwise heat treatment, a rigid framework of macromolecules of the gluten matrix is formed with the formation of additional physicochemical bonds between the components of the biocomposite material due to the compaction of amino acid fragments, which ensures high resistance to static loads.

CHAPTER 5

FEATURES OF MODIFICATION OF BIOCOMPOSITE MATERIALS

5.1. Modification of biocomposites filled with wood flour with sodium sulfate

The formation of biocomposite samples based on the gluten matrix consisted in obtaining a homogeneous composition, which included wood flour and a modifying additive (sodium sulfate). Depending on the volume of samples, the quantitative content of components per 100 wt. part of gluten solution.

The viscosity of the gluten solution with a concentration of 50% is low, which has a positive effect on the wetting process of wood flour particles. However, due to the formation of a biocomposite material in a press form under the influence of a thermal field, the gluten solution is released due to intensive evaporation of moisture. At a gluten solution concentration of 40%, the particles of the filler are sufficiently wetted, thus the composition is homogeneous, which allows the composition to be pressed. Increasing the viscosity of gluten by more than 40% is impractical due to a decrease in moisture content, which complicates the wetting process and reduces the homogeneity of the composition.

The mixture of gluten granules and water is placed in an airtight container to avoid water evaporation and ensure a controlled viscosity. Next, the mixture of gluten granules and water is placed in a drying oven with a temperature of 50 °C for 40 minutes with subsequent mixing to ensure homogeneity of the solution.

The next stage of obtaining the composition was the preparation of a mixture of filler (wood flour) with a modifier (sodium sulfate powder) by mechanical mixing of the components. Next, a solution of gluten (35 mass parts) is added to the mixture, followed by mechanical mixing until the composition is homogeneous.

With an increase in the exposure time of the composition in the thermal field, the compressive strength of biocomposites increases, which is due to the gradual removal of moisture and the formation of additional physical and chemical bonds between the components of the system. The exposure time of 1 hour is insufficient, since the lowest

values of the compressive strength were obtained at a thermal field temperature of 130 °C (Figure 5.1). It is obvious that such a temperature-time mode of formation does not ensure the complete removal of moisture and the formation of a dense structure of the biocomposite material. An increase in the temperature of the thermal field to 170 °C provides an increase in the compressive strength under compression by 28-30%, which is due to a more intensive release of moisture.

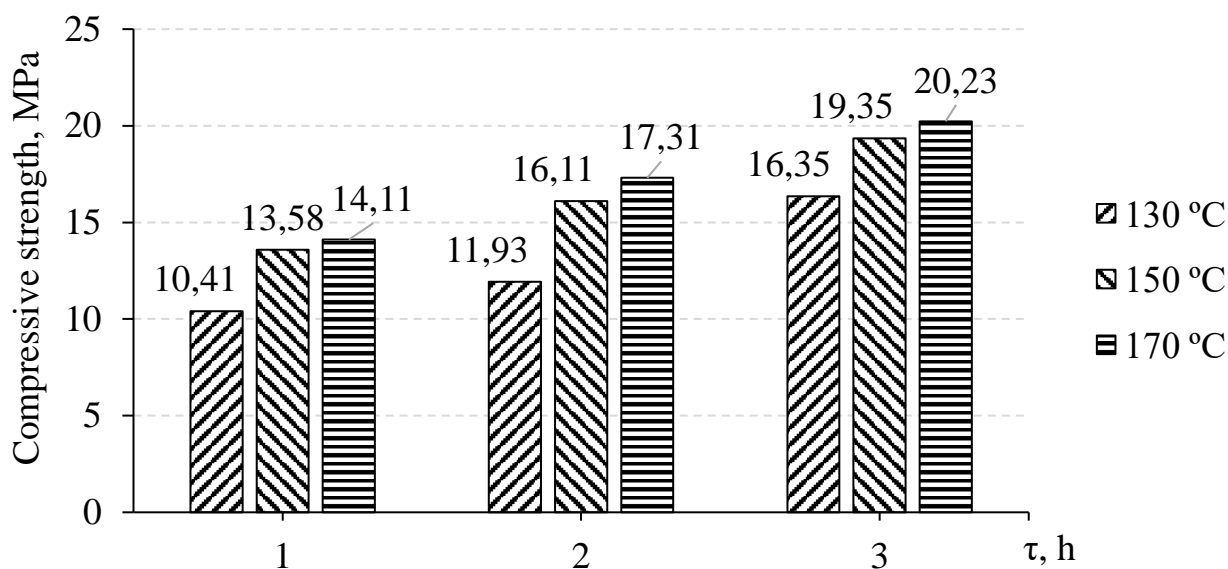


Figure 5.1. Dependence of the compressive strength of biocomposites on the temperature-time mode of formation

Exposure of biocomposite samples for 2 hours at a temperature of 130 °C allows to slightly increasing (12%) their compressive strength compared to exposure for 1 hour. However, increasing the temperature of the thermal field to 170 °C leads to an increase in this characteristic by 31-32% compared to a temperature of 130 °C. Increasing the exposure time to 3 hours provides an increase in the compressive strength of biocomposites (20.23 MPa). This is explained by an increase in the stiffness of the macromolecules of the biopolymer matrix due to the compaction of components and the formation of physical and chemical bonds. An increase in temperature leads to an intensive accumulation of thermal energy in the volume of biocomposites, which contributes to the maximum removal of moisture and uniform distribution of the biopolymer matrix.

In order to intensify the process of forming biocomposites in the thermal field, which has practical feasibility during the development of the technological process of forming products in production, a modifying additive (sodium sulfate) was used. A dosed amount of finely dispersed sodium sulfate powder is mixed with wood flour.

The composition is placed in a press form, compressed under a pressure of 10-15 MPa, fixed with punches to ensure a high density of the composition and avoid delamination. The degree of compression is determined by the content of the composition in the volume of the press form, which changed to regulate the amount of compaction of the composition. The thermal treatment of the composition in the press form was 2 hours at the optimal temperature of 150 °C, since the temperature of 170 °C led to the destruction of the surface layer of the samples due to the destruction of the organic component of the biocomposite material. After cooling to a temperature of 18-20 °C, the product removed from the press form. The optimal content of the composition in the cavity of the mold was determined using different ratios of the mass of the composition to the constant volume of the cavity ($V=9.5 \text{ cm}^3$) of the press form: 10 g, 11g, 12 g, 13 g. In the case of a small content of the composition in the press form (10 g), the pressing pressure was 10 MPa. The obtained biocomposite has a distorted shape, which caused by a large shrinkage due to intensive removal of moisture. In the case of loading 11 g of the composition, the pressing pressure was 12 MPa, which ensured the formation of a briquette with a small number of cracks. Increasing the pressing pressure to 15 MPa in the case of loading 13 g of the composition leads to formation of deep transverse surface cracks due to the destruction of weak physical bonds between the glutinous matrix and wood flour particles.

Therefore, it is more appropriate to load 12 g of the composition into a press form corresponding to a pressure of 13 MPa. This ensures the formation of a defect-free structure with a high degree of compaction and low residual tensions.

Introduction to the composition of 16 wt. part of the modifying additive provides an increase in compressive strength under compression to 30.44 MPa (Figure 5.2). The compressive strength of these biocomposites is 46% higher compared to the unmodified system. Contains 50 wt. part of the modifying additive increases the compressive

strength of biocomposites to 50.95 MPa, which is due to the hygroscopicity of sodium sulfate, because water molecules are absorbed and its content in the composition decreases. This ensures intensive formation of physical and chemical bonds between the components of the biocomposite material. When the content of sodium sulfate increases to 83 mass parts, there is a sharp (by 65-67%) decrease in strength under compression to 17.51 MPa, compared to the strength limit values of biocomposites containing 50 mass parts of sodium sulfate. This is explained by the intensive removal of water from the glutinous binder, which causes significant shrinkage of the biocomposite samples due to heat treatment and the appearance of micropores and microcracks on the surface of the samples. Destruction of biocomposite samples with sodium sulfate content of 83 mass parts occurs quickly with the formation of a brittle fracture zone, which caused by increased tensions due to the intensive structuring of the biopolymer matrix.

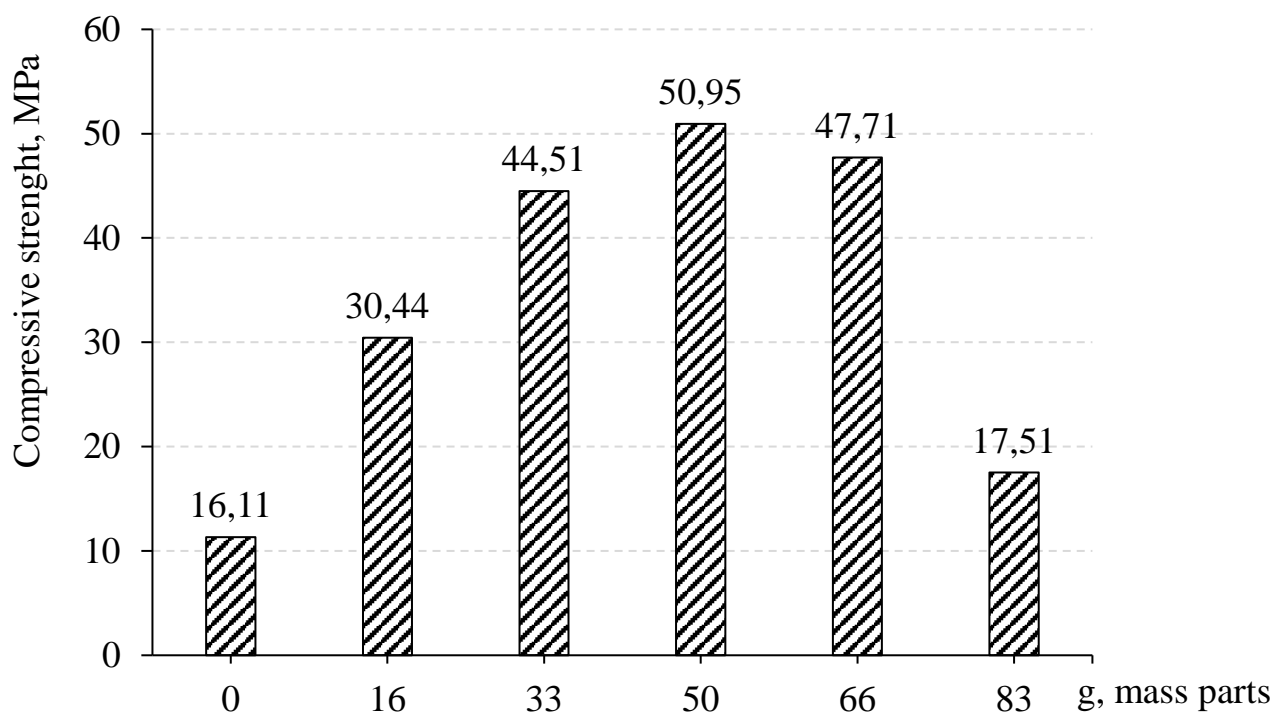


Figure 5.2. Dependence of the strength of biocomposite materials on the content of the modifying additive (sodium sulfate)

The fracture surface of biocomposite samples without a modifying additive is heterogeneous, with a sharp transition in places where the direction of crack propagation changes, which indicates increased fragility of the system (Figure 5.3, a). In the case of introducing a modifying additive into the composition of the biopolymer matrix under the influence of dynamic load, viscous destruction of the material occurs (Figure 5.3, b). This is due to the formation of additional physical and chemical bonds between gluten macromolecules, as well as between active groups of amino acids and the surface of wood flour particles. This mechanism of interaction of components is activated because of exposure to sodium sulfate, which adsorbs moisture and forms sodium sulfate decahydrate.

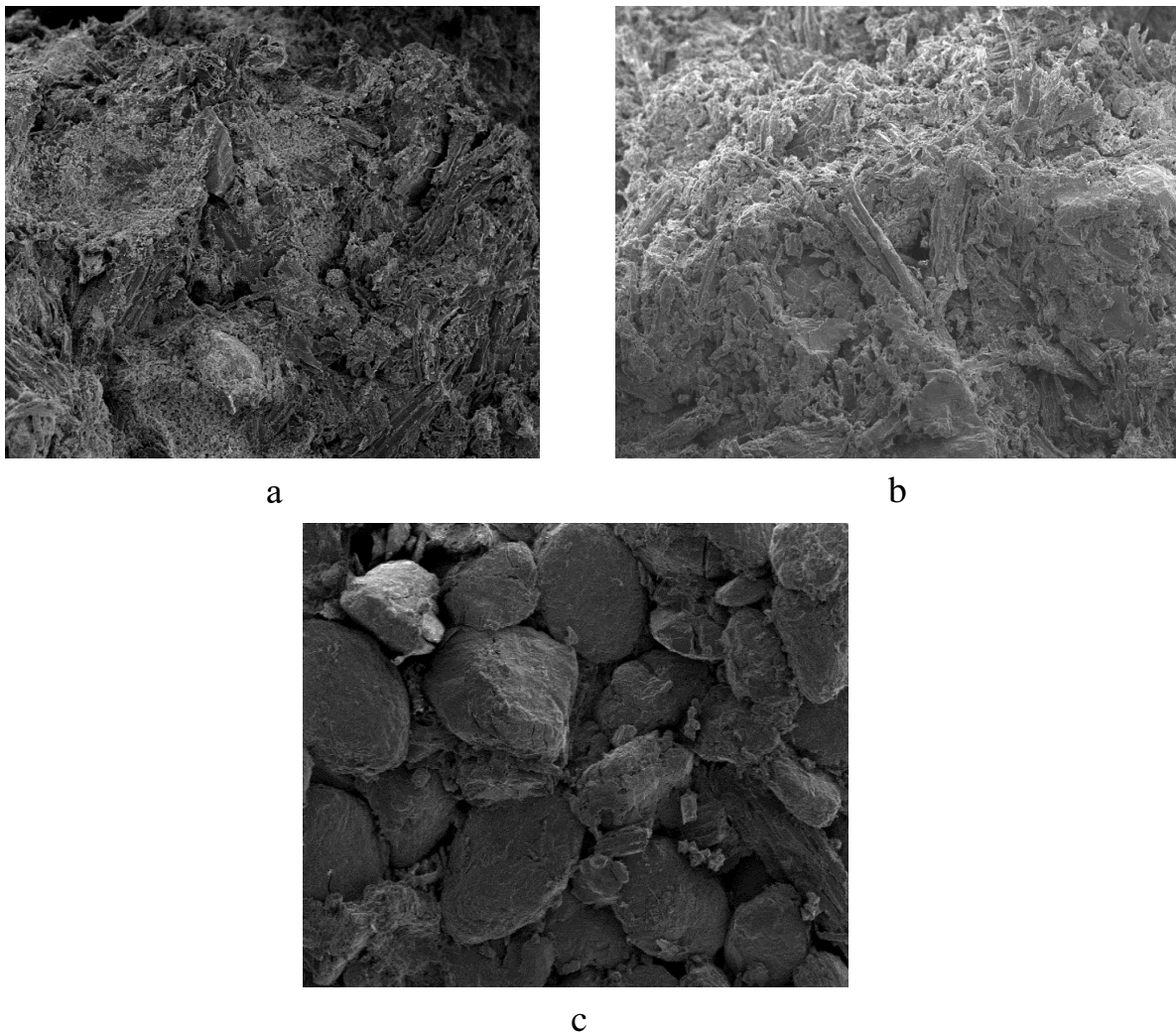


Figure 5.3. Fractograms of biocomposite materials based on a glutinous matrix filled with wood flour and modified with sodium sulfate in the amount:
a – without modifier, b – 50 mass parts, c – 83 mass parts, $\times 500$

On the fractogram of the biocomposite material containing 83 mass parts of sodium sulfate, there are crystals of the substance with rounded edges due to the destruction of the edges in the process of mechanical mixing of the components. It was established that this content of the modifying additive is excessive, since the dissolution of part of the crystals in the biopolymer matrix does not occur. As a result, the structure of the biocomposite is formed with increased heterogeneity in the form of clusters of deformed sodium sulfate crystals (Figure 5.3, c), which leads to material cracking due to the presence of microcracks and delaminations. Crystals of sodium sulfate do not get wet and are not fixed in a biopolymer binder, so they easily separate from each other and from the glutinous matrix under the influence of mechanical loads. This leads to the rapid propagation of cracks and the formation of a biocomposite material structure with low resistance to dynamic loads.

Conclusions. The optimal pressing pressure of the composition in the press form is 12 MPa, which ensures the formation of a defect-free structure of the biocomposite material with a high degree of compaction and low residual tensions.

The maximum duration of exposure of biocomposite materials without modifying additives in a thermal field at a temperature of 150 °C is 3 hours. This ensures complete removal of moisture from the volume of the biocomposite and the formation of products with sufficient strength due to increasing of stiffness of biopolymer matrix.

Introduction of a modifying additive (sodium sulfate) in the optimal amount of 50 mass parts provides an increase in the strength limit under compression to 50-52 MPa as a result of the formation of a homogeneous structure due to the formation of physical and chemical bonds between the components of the biocomposite material. This mechanism of interaction is realized due to the creation of favorable conditions due to a decrease in the water content in the glutinous binder, since sodium sulfate crystals adsorb water, which reduces the duration of heat treatment of products by 35%.

5.2. Modification of biocomposites filled with coffee grounds with sodium sulfate

At the first stage of obtaining biocomposite products of the required color spectrum, it is necessary to ensure the formation biocomposites of white color. Then it is easy to change the color of the product by introducing the necessary dye in the form of a powder additive. If the composite is not white, then the introduction of dye will not provide a high-quality decorative appearance of the product.

Biocomposite materials containing coffee grounds treated with an antiseptic change the color of the composition during formation, although the color of the filler is white (Figure 5.4). This is due to the presence of a biopolymer matrix based on bone glue (it has a dark color), which makes it difficult to form products with a controlled decorative appearance. Main cracks are recorded on the surface of the sample, which penetrate deeply into the material. The appearance of cracks is due to intensive heat treatment of the composition, which contains moisture in the coffee grounds particles, since this filler is characterized by hydrophilicity and the ability to retain water. This leads to a complete loss of the structural strength of the material, since under a slight mechanical load, destruction will occur by shifting the layers of the material along the formed cracks.



Figure 5.4. Biocomposite sample without dye (TiO_2)

Titanium dioxide is widely used in the chemical and food industries. It is inert and has a white color, which allows you to give the substance a white color. The

introduction of a dye in the form of a highly dispersed powder of titanium dioxide (TiO_2) into the composition of the biocomposite ensures a gradual transition from dark brown color to white (Figure 5.5, 5.6) in the case of an increase in the content of the additive in the composition from 3.3 mass parts up to 33.3 mass parts. At the same time, the content of the biopolymer matrix of a dark color decreases, which ensures the achievement of the required color.

The introduction of finely dispersed powder of titanium dioxide leads to a change in the structuring process, as additional physical bonds formed between the components of the biocomposite material. In the case of a content of 3.3 mass parts of the additive, there is a significant change in color and the formation of material with a smaller number of main cracks, which increases the structural strength of the products (Figure 5.5, a). Content 6.6 mass parts of titanium dioxide does not ensure the formation of the material without the appearance of main cracks, although such a crack was formed only one and not of a large length, which indicates the positive effect of the additive on the structuring of the biocomposite material (Figure 5.5, b).

On the peripheral part of the biocomposite sample containing 10 wt. of titanium dioxide, a small crack was recorded (Figure 5.5, c), which was formed as a result of the localization of inhomogeneity, which is associated with insufficient mixing of the system components. Introduction of 13.3 mass parts of dye ensures the formation of a biocomposite without structural defects. However, the end surface of the samples contains a significant quantity of dark inclusions of the biopolymer matrix (Figure 5.5, d).

Increasing the dye content to 16.6 mass parts and 20 mass parts allows the structuring of biopolymer composites without cracks or macrodefects and provides a bright surface with minor inclusions of the biopolymer matrix. The matrix can be unevenly distributed if the composition is not sufficiently homogenized (Figure 5.5, e), or evenly distributed in the case of qualitative mixing of the system components (Figure 5.5, f). Increasing the content of titanium dioxide to 23.3 mass parts leads to obtaining similar results, since samples with a uniform distribution of components and the formation of a defect-free structure were obtained (Figure 5.6, a).



a



b



c



d



e



f

Figure 5.5. Macrostructure of biocomposites with reduced dye content (TiO_2):
a – 3.3 mass parts; b – 6.6 mass parts; c – 10 mass parts; d – 13.3 mass parts;
e – 16.6 mass parts; f – 20 mass parts

Introduction of 26.6 mass part of the dye is excessive, which affects the uniformity of its distribution. The peripheral part of the surface of the biocomposite sample has a more pronounced white color compared to the rest of the surface (Figure 5.6, b), which is determined by the complicated mixing of the components due to the increased viscosity of the composition, which contains a smaller quantity of the biopolymer matrix.

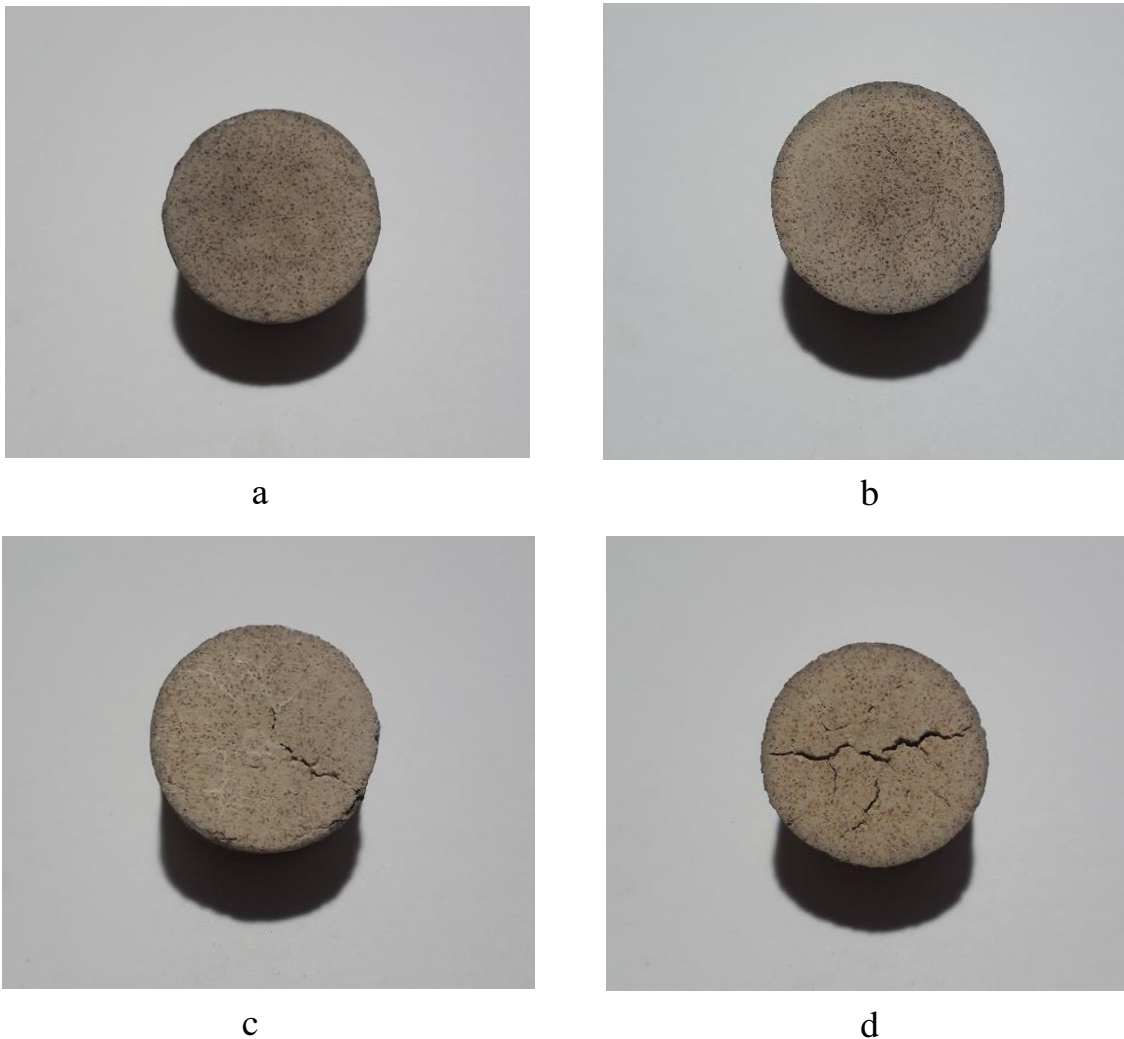


Figure 5.6. Macrostructure of biocomposites with reduced dye content (TiO_2):
a – 23.3 mass parts; b – 26.6 mass parts; c – 30 mass parts; d – 33.3 mass parts

Introduction of 30 mass part of the dye leads to the appearance of a main crack, which caused by a decrease quantity of biopolymer binder, because of which the filler and dye particles do not get wet. This leads to the destruction of physical bonds during heat treatment and the formation of delamination in the form of a crack (Figure 5.6, c).

Introduction of 33.3 mass part of the dye leads to the formation of biocomposites, on the surface of which there is one main crack, crossing the sample in diameter, and several smaller cracks (Figure 5.6, d). This indicates an insufficient content of the biopolymer binder, which is unable to form a continuous matrix.

Higher compressive strength was obtained for biocomposite samples, the heat treatment temperature of which without a press form was 50° C at the first stage compared to the temperature of 100° C. This is due to the uniform removal of moisture during heat treatment. In the case of applying a heat treatment regime with a temperature of 100° C, intensive removal of moisture occurs, which leads to the appearance of delaminations in the form of microscopic cracks, which significantly reduce the structural strength of biocomposites.

The highest compressive strength values (Figure 5.7) were obtained for biocomposites with a dye content of 23.3 mass parts. This is due to the optimal content of the dye, which takes part in the structuring of the biocomposite material. The dye particles are oxides that are evenly distributed in the volume of the biopolymer matrix and provide a decorative appearance to the material, as well as form physical and chemical bonds with the biopolymer matrix. The excess content of the dye reduces the compressive strength of biocomposites by 10%, which is due to a decrease in the wetting of the components by the biopolymer binder.

In the production process, an important aspect is the reduction of the duration of the formation of the material, which affects the cost price of the products. Therefore, it is expedient to use a modifying additive that is capable of intensifying the process of structuring a biocomposite material based on bone glue optimally filled with coffee grounds and dye. The use of sulfate salts ensures a uniform distribution of gluten macromolecules, which leads to the intensive formation of physical and chemical bonds between the components of the biocomposite material.

Sodium sulfate (Na_2SO_4) is a technologically convenient additive for the formation of biocomposite products. The use of sodium sulfate made it possible to reduce the duration of heat treatment to 30 min, but it is necessary to increase the temperature of heat treatment from 50° C to 100° C. In the case of biocomposites without sodium

sulfate, mainline cracks were formed. Much smaller cracks were formed in biocomposite samples (Figure 5.8, a) after the introduction of 3 mass parts additives.

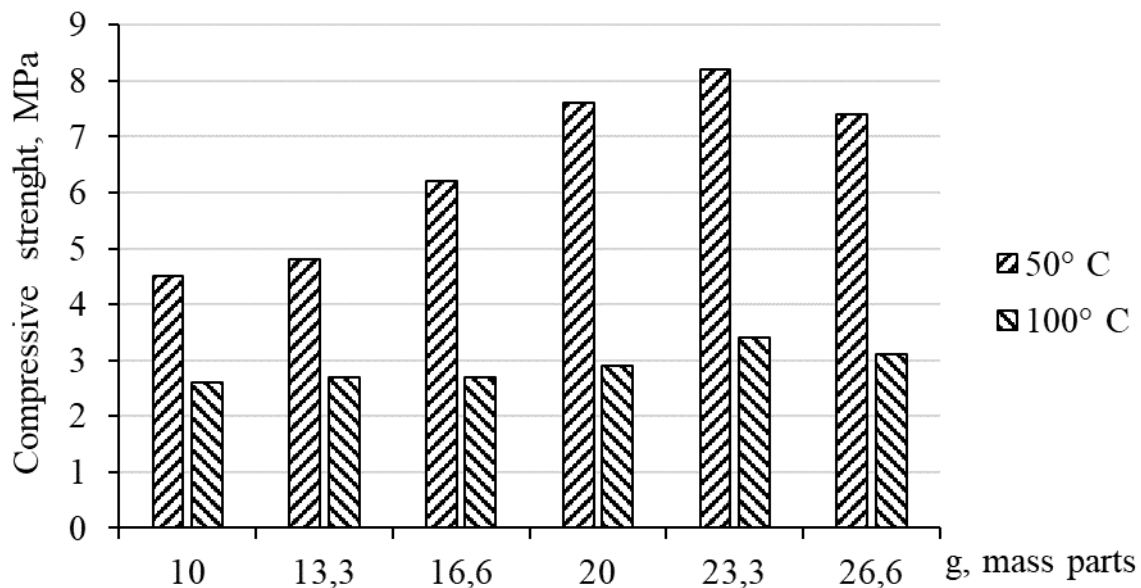


Figure 5.7. Compressive strength of biocomposites with dye content (TiO_2)

Introduction of 6 mass parts of the modifier allows to form biocomposite samples with inconspicuous cracks (Figure 5.8, b), which indicates the positive effect of the modifying additive. In case of introduction of 9 mass parts of sodium sulfate, no cracks were recorded on the surface of the biocomposite sample. However, there is a crater on the end surface, which formed because of tearing out part of the material (Figure 5.8, c). This happened due to the formation of physical and chemical bonds between the biopolymer matrix and the steel surface of the punch.

The use of sodium sulfate increases adhesive strength, which has a positive effect on the processes of structuring and forming bonds between the biopolymer matrix and filler particles. On the end surface of the biocomposite sample containing 12 mass parts of sodium sulfate, a large crater recorded (Figure 5.8, d). The crater was formed because of the destruction of the biocomposite with the formation of delamination in the surface part due to the predominance of adhesive strength over cohesive strength.



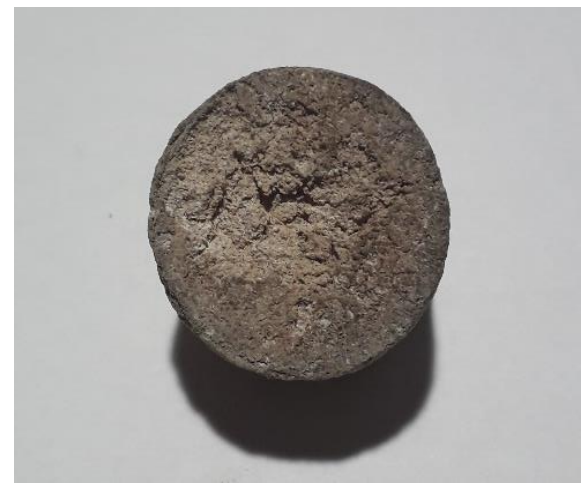
a



b



c



d



e

Figure 5.8. Macrostructure of biocomposites modified with sodium sulfate (Na_2SO_4):

a – 3 mass parts, b – 6 mass parts, c – 9 mass parts, d – 12 mass parts,

e – 15 mass parts

A similar situation was obtained for a biocomposite sample with a sodium sulfate content of 15 mass parts, that is, there is a destruction zone on the end surface (Figure 5.8, e). The reason for the appearance of the destruction zone is the formation of delamination in the surface part of the biocomposite.

Heat treatment of biocomposite materials containing sodium sulfate is advisable at a temperature of 100 °C. This modifier contributes to the uniform distribution of macromolecules of the biopolymer binder, which are capable of forming physical and chemical bonds between the surfaces of the filler particles at elevated temperatures. At a lower heat treatment temperature (50 °C), moisture remains in the biocomposite samples, which hinders the structuring process. Therefore, the compressive strength (Figure 5.9) and hardness (Figure 5.10) of biocomposites structured at a temperature of 100 °C is higher by 35-55% compared to the compressive strength of biocomposites structured at a temperature of 50 °C.

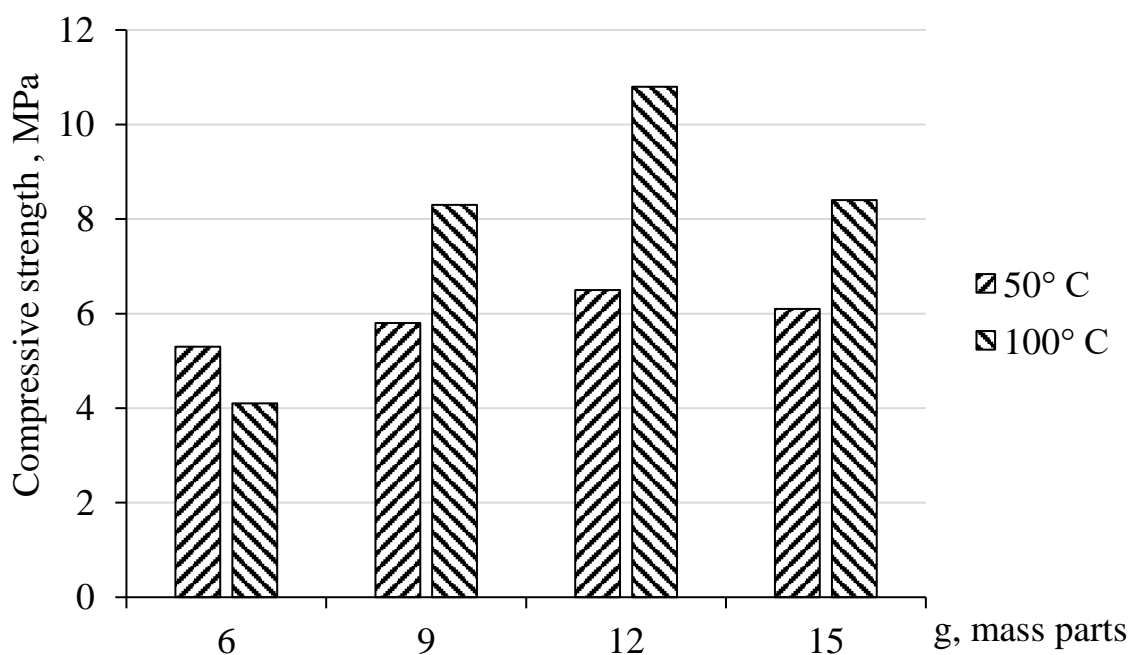


Figure 5.9. Dependence of compressive strength of biocomposites filled with sodium sulfate

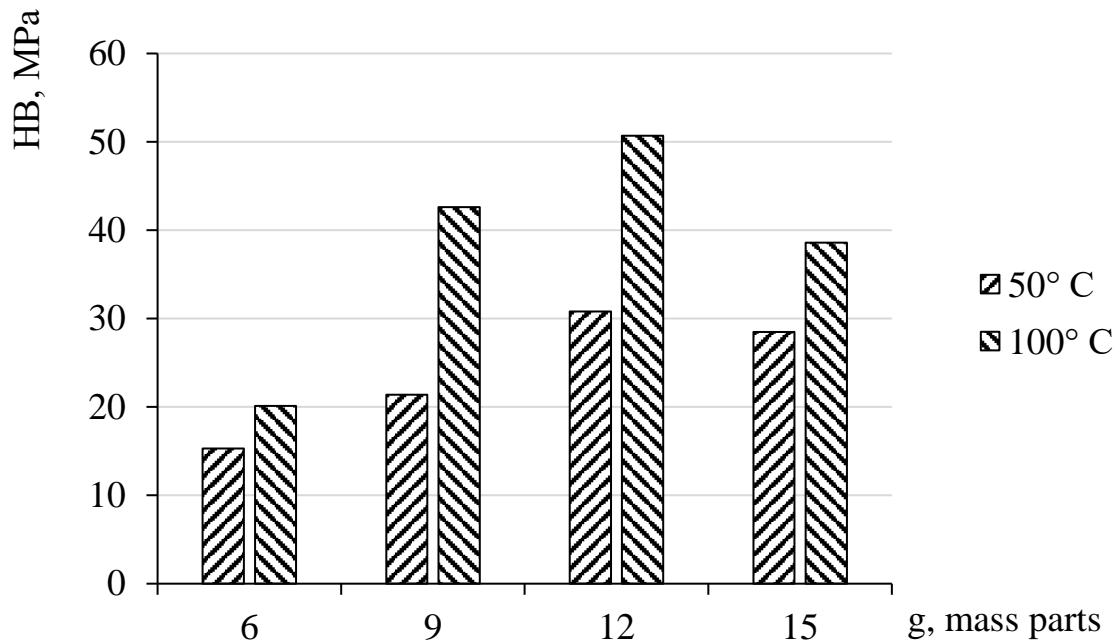


Figure 5.10. Dependence of the hardness of biocomposites filled with sodium sulfate

Conclusions. The use of coffee grounds treated with an antiseptic as a filler for biocomposite materials is ineffective due to the formation of a defective structure of the material because of intensive removal of moisture contained in the hydrophilic filler.

The introduction 13-26 mass parts of dye (TiO₂) into the composition ensures a change in the color of the biocomposite material, as well as the formation of defect-free products as a result of the formation of additional physical and chemical bonds between the biopolymer matrix and the surface of the dye particles.

An increase in the compressive strength occurs in the case of using 22-24 mass parts of dye, due to the introduction of an additional active filler, which performs a reinforcing function.

The use of 12 mass parts of sodium sulfate provides intensification of the structuring process of biocomposites due to the formation of a homogeneous structure. As a result, the duration of heat treatment was reduced by two times and the compressive strength increased by 25%.

The developed material is recommended to be used for the production of elements of furniture sets and interior decoration details of vehicles.

5.3. Modification of biocomposites filled with wood flour with polyvinyl acetate

The technological mode of forming biocomposite materials based on an aqueous solution of gluten, filled with wood flour powder, involves heat treatment of the composition at various stages. This is due to the excessive content of water in the composition, which ensures manufacturability for the uniform distribution of the binder in the volume of the material, but reduces the physical, mechanical and operational characteristics of the biocomposite material.

At the first stage, it is necessary to dry the composition to remove excess moisture, which ensures wetting of the filler particles with a glutinous binder. During heat treatment, water changes into a vapor state and evaporates. This leads to the release of part of the binder through the cracks of the press form and the formation of cavities inside the biocomposite material, which sharply reduces the strength of biocomposites. Therefore, it is advisable to remove moisture by drying the composition at a temperature of 50-60 °C for 10-20 minutes. At the same time, the composition loses its moisture content in the range of 3-9%, depending on the specified processing mode and the nature of the filler.

It is advisable to measure compressive strength after heat treatment of biocomposite samples in a press form. The composition is exposed to the heat field directly in the press form at a temperature of 140-150 °C for 30 minutes with the application of compressive force at an intermediate stage. The glutinous binder melts which wets the filler particles and is evenly distributed throughout the volume of the material. At a temperature of 110-130 °C, the duration of the forming process increases to 2-3 hours, which is inefficient due to the complication of the technological process. At a high temperature of 160-170 °C, the thermal destruction of the glutinous binder

occurs. There is also destruction of filler particles of organic origin. As a result, the surface layer becomes brittle and loses wear resistance.

The compressive strength of unmodified biocomposite samples, the composition of which was not dried, is 5.8-6.2 MPa at a temperature of heat treatment of the composition in the press form of 140 °C. Conducting heat treatment at a temperature of 150 °C allows to slightly increase (by 23-25%) the compressive strength (Figure 5.11) of biocomposites. This ensures a higher degree of dissolution of the glutinous binder due to obtaining a greater amount of thermal energy and a uniform distribution of the biopolymer matrix between the filler particles.

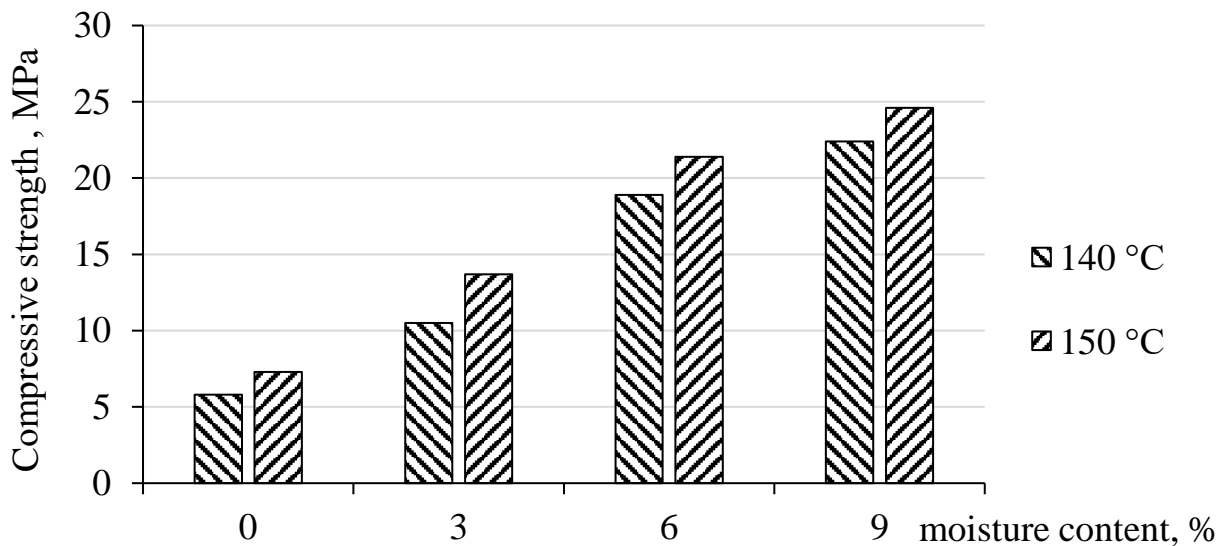


Figure 5.11. Dependence of the compressive strength of unmodified biocomposites depending on the moisture loss of the composition (TO_0) and heat treatment (TO_1 : $\tau=30$ min, TO_2 : $t=100$ °C, $\tau=60$ min)

If the composition loses 3% of moisture, the compressive strength increases by 43% and 46% for composites whose heat treatment temperature was 140 °C and 150 °C, respectively. This is due to the lower moisture content in the composition, because of which fewer cavities are formed during heat treatment.

Increasing the duration of drying ensures a loss of 6% of moisture. As a result, the compressive strength increases by 3 times compared to the composition with the

maximum moisture content. A further increase in moisture loss to 9% has a positive effect on the strength characteristics of biocomposites, as the material obtains maximum compressive strength values (24.6 MPa), which is determined by the optimal moisture content in the glutinous binder. At a degree of moisture loss of 10% and above, there is a sharp decrease in the manufacturability of the composition, which is associated with insufficient wetting by the binder of the filler. As a result, the particles are in mechanical contact without the formation of physical and chemical bonds.

A temperature of 150 °C provides higher compressive strength values, since a higher degree of thermal influence ensures high fluidity of the binder and better surface wettability of the filler particles.

An important factor affecting the strength characteristics is the duration of exposure of the composition in a thermal field at a temperature of 150 °C in a mold followed by heat treatment of biocomposites at a temperature of 100 °C for 60 minutes. Unmodified biocomposite materials without drying with exposure in the mold for 30 min (7.3 MPa) have the lowest values of compressive strength, which is associated with a high moisture content in the composition and insufficient time to complete the process of uniform distribution of the binder in the volume of the material (Figure 5.12).

Increasing the exposure time of biocomposites to 40 min without drying the composition allows increasing the compressive strength by 36%. Increasing the duration of exposure for every 10 minutes provides an increase in this characteristic by 27-37%, which is due to a longer time of heat exposure to the composition. This is explained by the more intense processes in the system, which are associated with the redistribution of the binder and the reduction of moisture in the composition. Increasing the duration of exposure of biocomposites in a press form more than 60 minutes is impractical, since there is no significant increase in strength, but at the same time, the technological process of forming products is complicated.

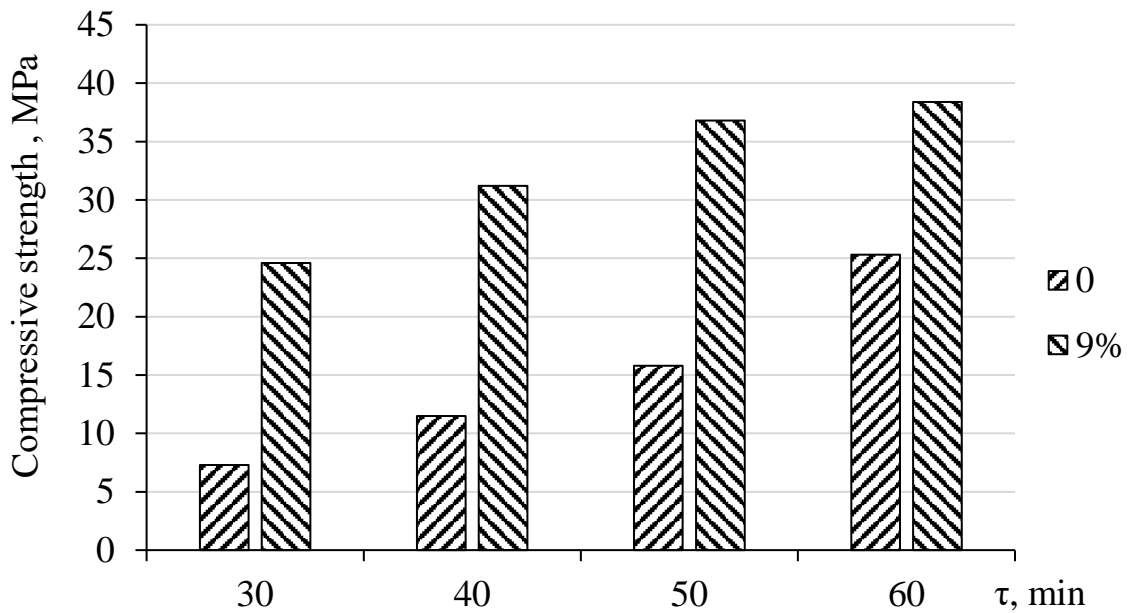


Figure 5.12. Dependence of the compressive strength of unmodified biocomposites depending on the exposure of the composition in a press form (TO_1 : $t=150\text{ }^{\circ}\text{C}$) and without a press form (TO_2 : $t=100\text{ }^{\circ}\text{C}$, $\tau=60\text{ min}$)

Drying the composition to a moisture loss of 9% provides increase in compressive strength of biocomposites by 3.4 times compared to biocomposites whose composition was not dried. Low compressive strength values are determined by the excess moisture contained in the composition and not completely removed from the material due to the high tightness of the press form and insufficient exposure time in the thermal field.

Increasing the duration of exposure in the press form at a temperature of $150\text{ }^{\circ}\text{C}$ significantly increases the compressive strength, since the dissolution of the glutinous matrix also occurs with a lower moisture content in the composition. However, at the same time, the remaining moisture removed from the material in a similar period of time, the total amount of which in the system lower compared to biocomposites whose compositions were not dried.

The highest values of compressive strength (38.4 MPa) were obtained for biocomposites, the duration of which kept in the mold at a temperature of $150\text{ }^{\circ}\text{C}$ for 60 minutes. This is explained by the need to keep the composition in the thermal field longer to complete the processes of redistribution of the binder with limited moisture

content, which complicates the processes of the transition of the binder into a liquid state.

In the solid state, gluten is a brittle material with high hardness and rigidity. This type of matrix is quite suitable for the formation of structural products that exposed to static loads. However, at the same time, it is important to evaluate the possibility of increasing resistance to dynamic loads in order to expand the scope of introduction of products based on glutinous biocomposites. The glutinous matrix dissolves in water. Therefore, for modification, it is advisable to use a substance that also dissolves in water and is environmentally safe. Polyvinyl acetate, which has high technological characteristics, meets these requirements. Polyvinyl acetate is soluble in water and environmentally safe. In this case, it is necessary to establish the optimal content of the additive in the system and the mode of formation of modified biocomposites.

This mode of heat treatment of biocomposites chosen taking into account the analysis of previous results: drying of the composition until the moisture loss is 9%, formation of products in a press form at a temperature of 150 °C for 60 minutes. At the same time, the system contains moisture, which localized mainly in the central part of the sample. There is a need to remove moisture, which reduces the strength of the biocomposite material, as the degree of rigidity of macromolecule chains decreases due to the presence of water molecules. Therefore, additional heat treatment (TO_2) of biocomposites is necessary, the mode of which must be determined experimentally.

In previous studies, the temperature of additional heat treatment of biocomposites was 100 °C for 60 minutes. However, the biocomposite system did not contain a modifying additive and the behavior of the material at another temperature, which is lower or higher than the temperature of 100 °C, was not investigated.

When a small quantity of polyvinyl acetate (2%) introduced, a significant increase in compressive strength of biocomposites does not occur compared to unmodified biocomposites. This increase is 10-12%, since the content of the modifying additive is insignificant (Figure 5.13). Lowering the temperature of additional heat treatment to 50 °C of biocomposites with a polyvinyl acetate content of 2% reduces the compressive strength to 5-6 MPa. This is explained by the insufficient thermal effect, which does not

ensure the removal of moisture from the volume of the material. The absence of additional heat treatment allows obtaining compressive strength at the level of 2-3 MPa, which is unacceptably low values for a material of structural purpose. Increasing the heat treatment temperature to 150 °C allows obtaining the maximum values of compressive strength (56-57 MPa), which is due to the low moisture content and the formation of a biopolymer matrix with a high degree of rigidity of the framework of gluten macromolecules.

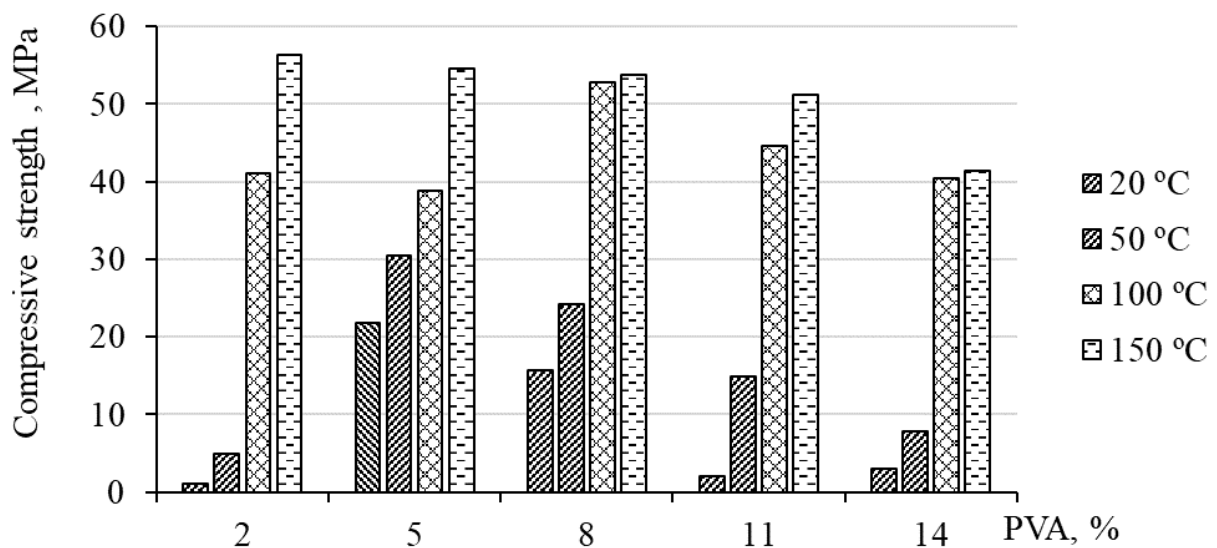


Figure 5.13. Dependence of the compressive strength of biocomposites modified with polyvinyl acetate on the temperature of additional heat treatment

The introduction of 5% of the modifying additive leads to a slight decrease in the compressive strength of biocomposites, the temperature of which was additionally heat treated at 100 °C and 150 °C. However, the strength of biocomposites without additional treatment increased by 10 times and by 6 times for biocomposites, the temperature of which was heat treated at 50 °C. This is explained by the higher content of polyvinyl acetate, which is able to form bonds with the surface of wood flour particles.

The introduction of 8% of the modifying additive leads to a 30% increase in the compressive strength of biocomposites compared to a polyvinyl acetate content of 5% at an additional heat treatment temperature of 100 °C. This is due to the optimal heat treatment temperature, which makes it possible to obtain a homogeneous mixture of

solution of gluten and polyvinyl acetate. The optimal ratio of the components of the binder ensures the formation of a framework of chains of macromolecules with their uniform distribution and the formation of the maximum number of physical and chemical bonds between the components. Additional processing at lower temperatures of 20 °C and 50 °C leads to a decrease in the compressive strength limit, since at such temperatures the formation of a homogeneous solution based on gluten and polyvinyl acetate does not occur.

The introduction of 11% and 14% of the modifying additive leads to a uniform decrease in compressive strength by 12-15% at heat treatment temperatures of 100 °C and 150 °C. Application of additional heat treatment at temperatures of 20 °C and 50 °C reduces the compressive strength of biocomposites by 40-45%. A significant decrease in compressive strength at lower temperatures (20 °C and 50 °C) is due to insufficient thermal energy, which does not ensure the transition of polyvinyl acetate into a liquid state and obtaining a homogeneous solution of the binder components.

Biocomposite materials with a low content of modifying additive (2%), which are thermally treated at a temperature of 20 °C, have quite high values of impact viscosity (3.7 kJ/m²), which is due to the presence of polyvinyl acetate macromolecules in the composition of the biopolymer matrix (Figure 5.14). Macromolecules of the modifier provide a higher viscosity of the system compared to macromolecules of gluten, which characterized by high fragility. The segments of the chains of polyvinyl acetate macromolecules form a mechanical mixture with the interweaving of the chains of the components of the binder, which increases the system's resistance to the influence of dynamic loads.

At a temperature of 20 °C, the biocomposite system contains an excess amount of moisture, which reduces the stiffness of the segments of gluten macromolecules and ensures the flexibility of the chains of the biopolymer system. As the temperature rises to 50 °C, moisture removed from the volume of the material, resulting in an increase in the stiffness of the biopolymer matrix and a 20% decrease in the impact strength of the material. Increasing the temperature to 150 °C leads to the formation of a system with a similar structure and ability to resist dynamic loads.

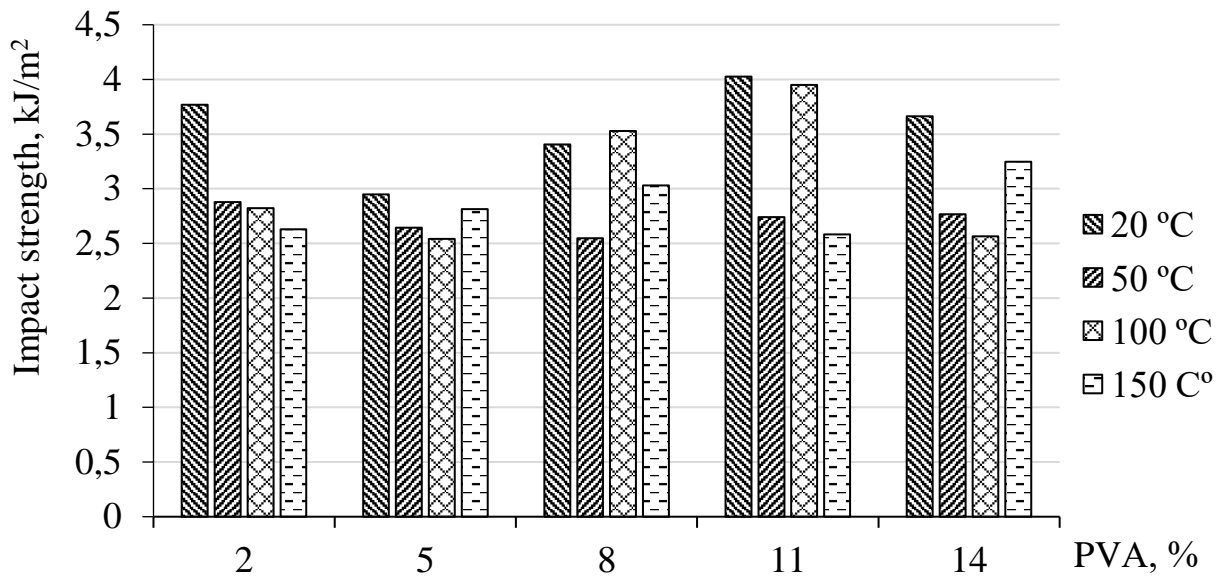


Figure 5.14. Dependence of the impact strength of biocomposites modified with polyvinyl acetate on the temperature of additional heat treatment

The introduction of 5% polyvinyl acetate leads to the formation of biocomposite materials also with low resistance to dynamic loads (2.5-2.9 MPa), which is explained by the dominant effect on the formation of the structure of the biopolymer matrix of gluten macromolecules. At a temperature of 20 °C, there is excess moisture in biocomposites with a polyvinyl acetate content of 5%, which ensures partial dissolution of the biopolymer matrix and reduces resistance to dynamic loads. Increasing the content of the modifying additive to 8% leads to the formation of biocomposites with higher impact strength, which is associated with the effect of polyvinyl acetate on the formation of the structure of the biopolymer matrix. Polyvinyl acetate macromolecules have increased flexibility compared to the glutinous binder, which in the total effect provides higher resistance to the destruction of the system.

The introduction of 11% of the modifying additive provides the highest values of the impact viscosity of biocomposites, which is due to the optimal content of polyvinyl acetate. Macromolecules of the modifying additive form a homogeneous framework with the glutinous biopolymer. This framework provides effective energy absorption of dynamic loads without destroying physical and chemical bonds. The introduction of

14% of the modifying additive does not provide an additional increase in impact strength, since the excess content of polyvinyl acetate leads to plasticization of the biopolymer matrix, which has low values of mechanical characteristics.

Bicomposites without drying after the main heat treatment have a brittle nature of destruction with the formation of an almost straight edge along the propagation of the crack, which is formed as a result of dynamic loading (Figure 5.15). The deviation of the direction of crack propagation for biocomposites with a content of 2% polyvinyl acetate relative to the load vector is 5° (Figure 5.15, a). With an increase in the content of the modifying additive to 8%, the deviation increases to 8° . This indicates a significantly greater deviation (37%) of the crack propagation direction due to obstacles in the form of dense inclusions of a solid mixture of components of the biopolymer matrix (Figure 5.15, b). With a higher content of polyvinyl acetate, the deviation is 10° (Figure 3.15, c), which is associated with a higher number of local volumes with an increased density of the biopolymer matrix. With a polyvinyl acetate content of 14%, the deviation decreases, because more uniform structure is formed (Figure 5.15, d).

The deviation of the direction of crack propagation relative to the vector of load action for biocomposites with a content of 2% modifying additive and additional heat treatment at a temperature of 50°C is 5° . Biocomposites with a modifier have a crack propagation pattern similar to biocomposites without additional heat treatment (Figure 5.16, a). Biocomposites with a polyvinyl acetate content of 8% (TO_2 : $t=50^\circ\text{C}$) have a slight (3°) deviation in the direction of crack propagation, which is associated with the loss of material moisture due to increased temperature and the formation of a structure with increased fragility (Figure 5.16, b).

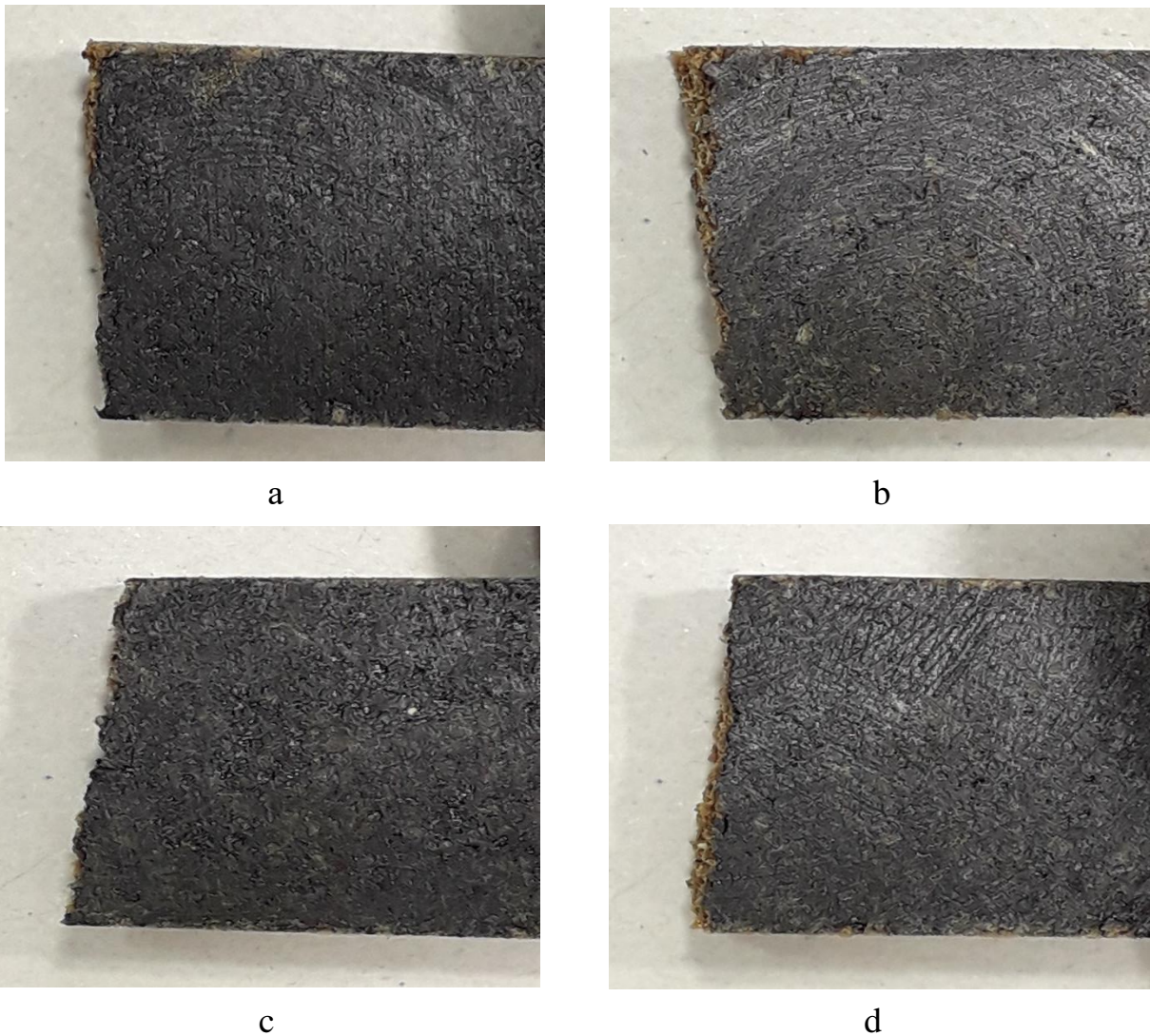


Figure 5.15. Macrostructure and nature of fracture of biocomposites without additional heat treatment (TO_2) with polyvinyl acetate content:
a – 2%; b – 8%; c – 11%; d – 14%

An increase in the temperature of additional heat treatment of biocomposites with a higher content of polyvinyl acetate (11%) leads to the formation of a dense structure with a local arrangement of areas that cause a deviation of the crack propagation to an angle of 12° (Figure 5.16, c). With a modifying additive content of 14%, the direction deviation is 10° , which is due to the formation of a structure with a higher degree of flexibility of the framework of macromolecules (Figure 5.16, d).

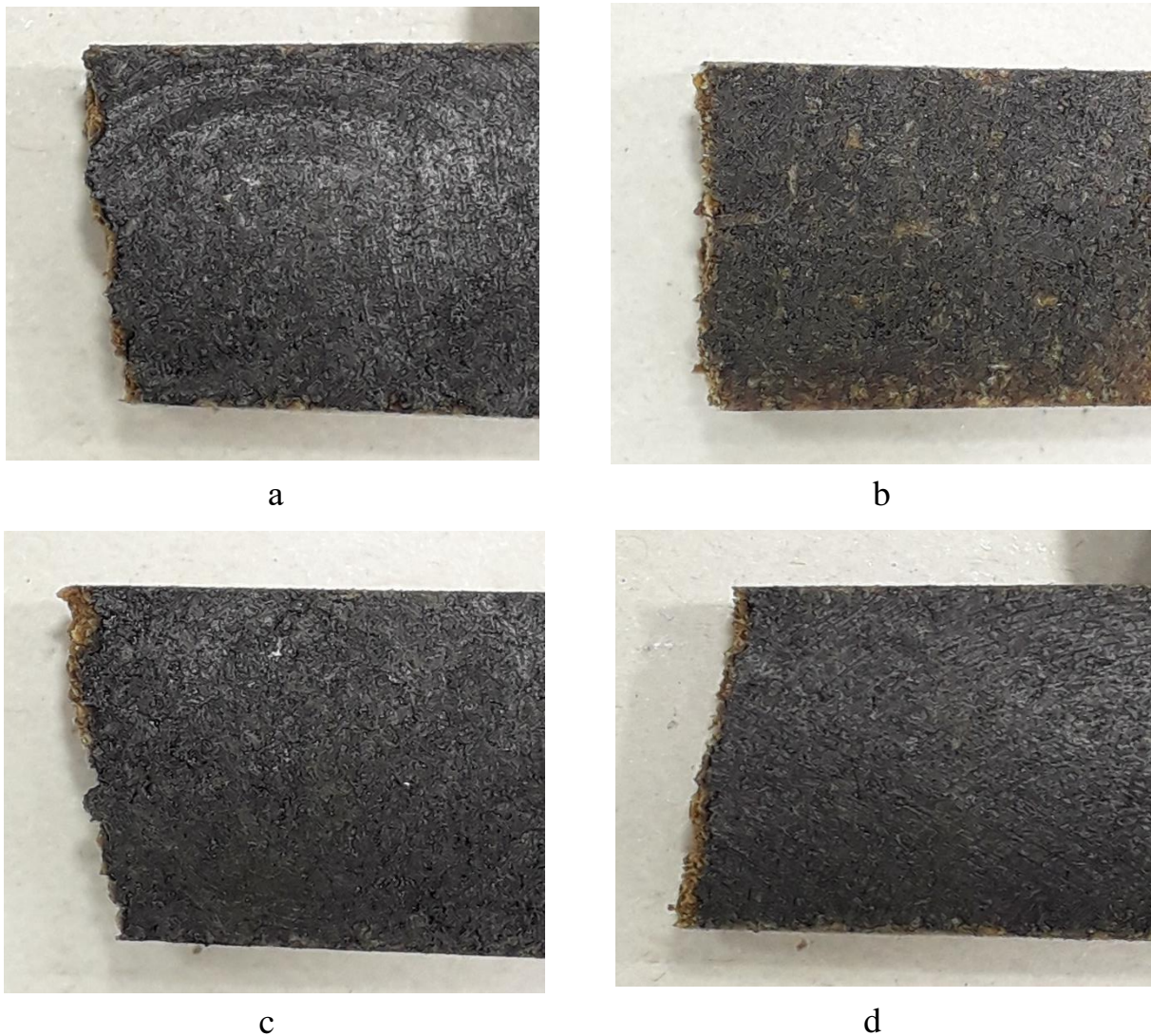


Figure 5.16. Macrostructure and nature of fracture of biocomposites thermally treated at a temperature of 50 °C with polyvinyl acetate content:

a – 2%; b – 8%; c – 11%; d – 14%

Biocomposites with a minimum content of a modifying additive (2%) after additional heat treatment are fragile, since the deviation of the crack propagation direction does not exceed 5° (Figure 5.17, a). The fragility of the system increases in case of fracture of biocomposites with a content of 8% modifying additive, since the deviation of crack propagation is 2° (Figure 5.17, b). This is due to the processing of biocomposites at a temperature of 100 °C, which ensures a decrease in moisture content and an increase in the rigidity of the biopolymer matrix framework.

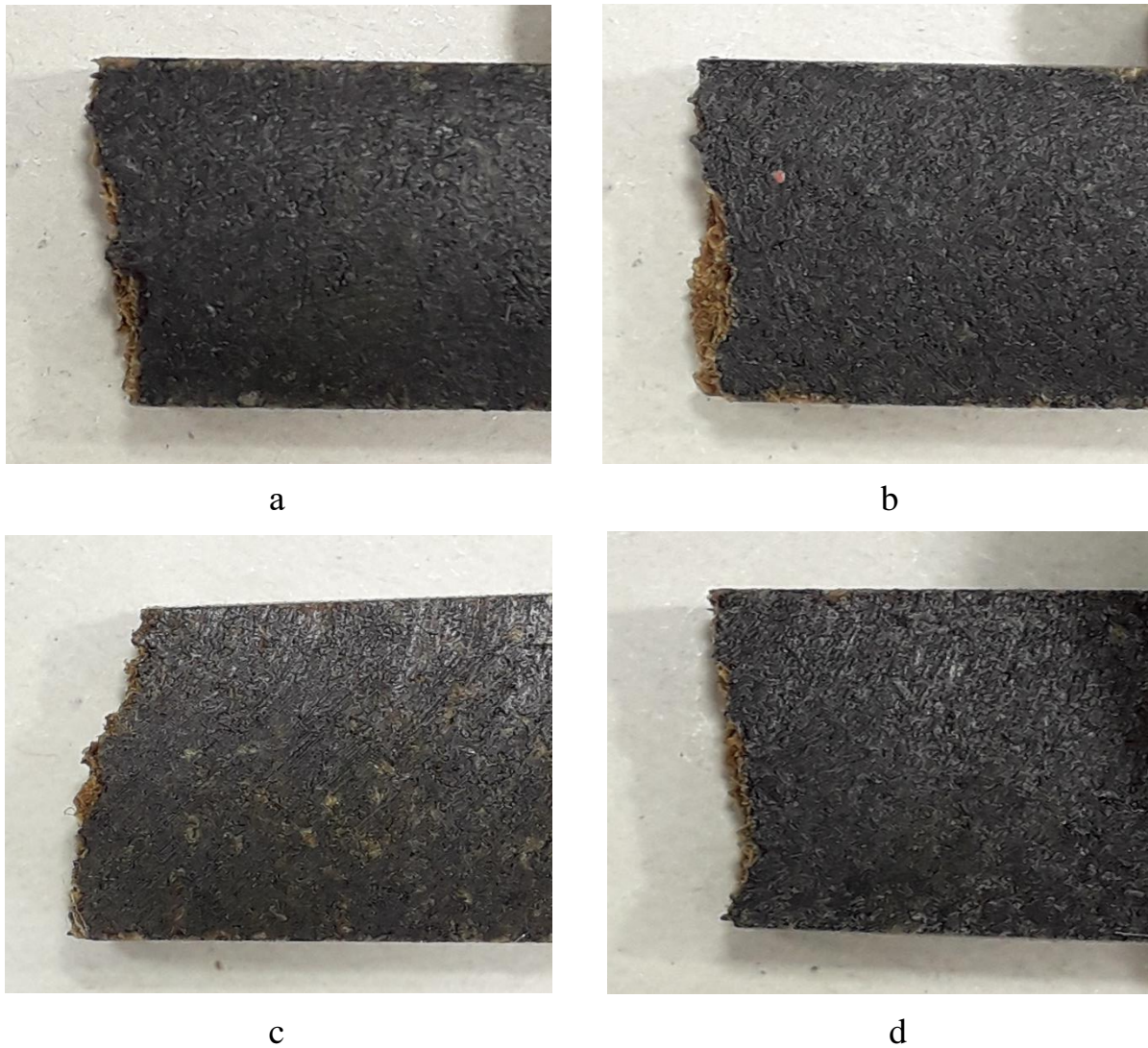


Figure 5.17. Macrostructure and nature of fracture of biocomposites thermally treated at a temperature of 100 °C with polyvinyl acetate content:
a – 2%; b – 8%; c – 11%; d – 14%

For the fracture of biocomposites with a polyvinyl acetate content of 11%, it is necessary to apply more energy, since the propagation of crack occurs with a deviation of 15° (Figure 5.17, c). This is due to the formation of additional physical and chemical bonds between components of biopolymer matrix. Increasing the modifying additive to 14% leads to a decrease in the crack propagation deviation (7°). This indicates a decrease in the resistance of the system to the influence of dynamic load due to the excess content of polyvinyl acetate, which plasticizes the matrix (Figure 5.17, d).

Additional heat treatment at a temperature of 150 °C of biocomposites with a polyvinyl acetate content of 2% does not provide a significant increase in the material's

resistance to dynamic loads, since there is no deviation in crack propagation (Figure 5.18, a). This indicates a high degree of rigidity of the framework of macromolecules because of the consumption of moisture by the system.

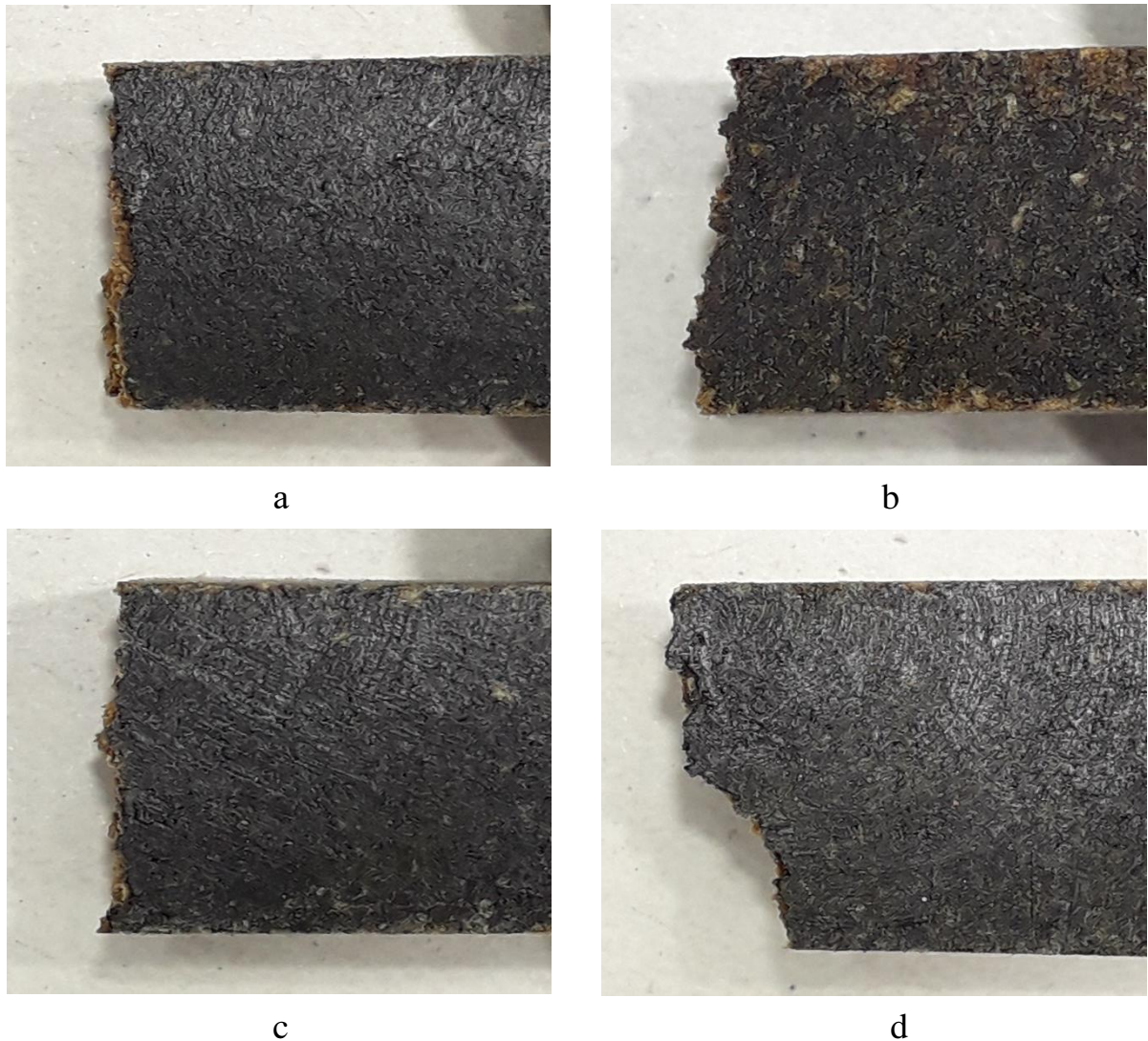


Figure 5.18. Macrostructure and nature of fracture of biocomposites thermally treated at a temperature of 150 °C with the content of polyvinyl acetate:

a – 2%; b – 8%; c – 11%; d – 14%

Increasing the content of the modifying additive to 8% and 11% ensures an increase in the impact viscosity of the material, since the deviation is 6° and 3°, respectively (Figure 5.18, b, c). This is due to the presence of polyvinyl acetate macromolecules, which enhance the plasticizing effect.

The plane of crack propagation during the destruction of biocomposites with a polyvinyl acetate content of 14% has a complex topography due to the high content of the modifying additive. The deviation of the crack propagation direction is 18°, which indicates the formation of a structure resistant to the influence of dynamic loads (Figure 5.18, d). With an increased content of the modifying additive, additional physicochemical bonds formed, which determine the density of the biopolymer matrix and the nature of the material's destruction.

Conclusions. Biocomposites have the maximum values of compressive strength (24.6 MPa) due to the loss of 9% of moisture during preliminary heat treatment, because of which fewer cavities formed.

The highest values of compressive strength (38.4 MPa) were obtained by biocomposites with a duration of exposure in a mold at a temperature of 150 °C for 60 minutes. This is explained by the need for long exposure of the composition in a thermal field to complete the processes of redistribution of the glutinous binder with a low moisture content.

The compressive strength of biocomposites containing polyvinyl acetate (5%) without additional heat treatment increased by 10 times and by 6 times for biocomposites treated at a temperature of 50 °C. This is explained by the higher content of polyvinyl acetate, which is able to form bonds with the surface of wood flour particles.

The introduction of 11% of the modifying additive provides the highest values of the impact viscosity of biocomposites, which is due to the optimal content of polyvinyl acetate. Macromolecules of the modifying additive form a homogeneous framework with the glutinous biopolymer.

The plane of crack propagation during the destruction of biocomposites with a polyvinyl acetate content of 14% has a complex topography due to the high content of the modifying additive. The deviation of the direction of crack propagation is 18°, which indicates the formation of a dense structure resistant to the influence of dynamic loads.

CHAPTER 6

DEVELOPMENT OF RECYCLING TECHNOLOGY OF BIOCOMPOSITE PRODUCTS

Secondary raw materials from biocomposite products based on a solution of glutin and wood flour are obtained by the combined method of exposure to various energy fields as a result of the following operations: crushing to obtain large products, absorption of water by the biocomposite product, grinding to obtain small products, drying, sieving. The first stage of recycling consists in crushing in order to separate the product into large parts (Figure 6.1, a) using a knife-type shredder.

The next stage involves immersing the products in water heated to 80 °C, which is in a heat-insulating vessel, for 30-60 minutes, depending on the size of the pieces. As a result, the biopolymer matrix is heated, and the binder and filler are saturated with water molecules, which ensures the destruction of interphase bonds and easy separation of components. It is difficult to carry out further grinding in the mill due to the particles sticking together, so the moistened pieces are dried in a drying cabinet at a temperature of 100-140 °C for 5-10 minutes in order to remove excess water content. Small fractions are obtained as a result of mechanical grinding using a hammer-type mill with high-frequency rotation of the cutting tool (Figure 6.1, b). Classification of the powder product is performed using sieves with a given hole diameter in the range of 0.4-0.6 mm (Figure 6.1, c). The finished product is a powder made of particles of the same size (Figure 6.1, d), which is suitable for use as a filler for biocomposite materials.

The formation of biocomposite materials from primary raw materials takes place taking into account the manufacturability of the composition, provided that the particles of the filler are completely wetted at the limit content of the glutin solution (40%) (Figure 6.2). With such a ratio of components, the maximum value of the compressive strength limit (10.4 MPa) of the biocomposite material is reached.



a



b



c



d

Figure 6.1. The general appearance of secondary raw materials in the stages of the technological process: a – large pieces; b – grinding in a mill; c – the raw material for sieving; d – powder product

With a higher content of glutin solution (50%) during the main heat treatment of the biocomposite material, the solvent (water) is heated and evaporates, which leads to the intense release of the binder through the cracks in the mould. At the same time, the compressive strength of such biocomposites decreases by 2.5-3 times compared to biocomposites containing 40% glutin solution. With a lower content of the solution (30%), the filler is not completely wetted, so the formation of physical and chemical bonds between the biopolymer matrix and the surface of the filler is impossible or difficult. At the same time, the strength limit of such biocomposite materials is the lowest (1.8-2 MPa), since delaminations and cracks occur, and the wear resistance

decreases. The introduction of secondary raw materials in the amount of 60% and 40% glutin solution into the composition of the biocomposite material reduces the compressive strength by 45-50%, which is due to the high content of glutin solution in the composition. In the case of using secondary raw materials, the total glutin content is significantly higher compared to primary raw materials, because on the surface of wood flour particles obtained in the recycling process, there are adsorbed macromolecules of glutin and water, which are difficult to remove in the process of combined processing by hydro-mechanical influence of energy fields.

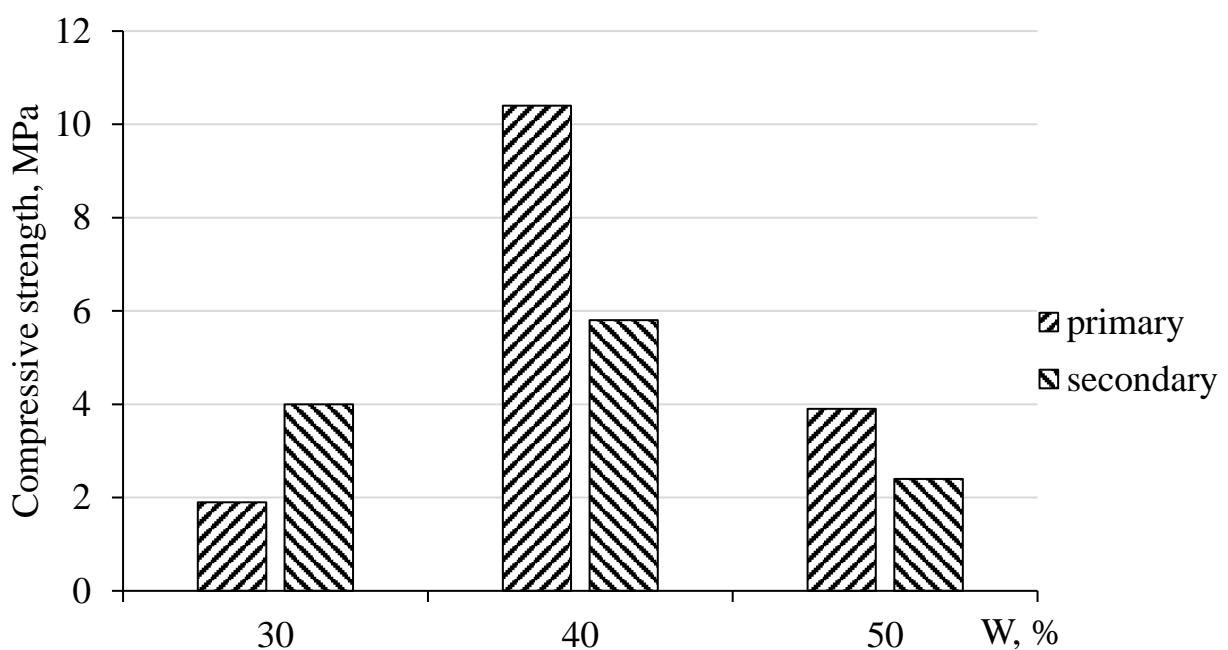


Figure 6.2. Dependence of the compressive strength limit of biocomposites on the content of glutin solution in the composition and the type of raw material

The use of a higher content of glutin solution (50%) leads, accordingly, to a reduction of the compressive strength limit by 38-45% compared to similar biocomposites made from primary raw materials. At the same time, the total content of glutin, which is contained in the pores of secondary raw materials and is additionally introduced during the formation process, increases, therefore plasticization of the biopolymer matrix occurs due to the excess moisture content in the biocomposite. In the case of introducing a glutin solution in the amount of 30%, the compressive strength

increases by 50-55% compared to a similar material containing a primary processing filler. This is due to the reduced content of the gluten solution, which is introduced during the preparation of the composition. At the same time, the total content of gluten is optimal compared to biocomposites, which contain an increased content of gluten solution of 40% and 50%. With this content, a structure with a higher rigidity of the biopolymer skeleton and the formation of an additional number of physicochemical bonds is formed. However, with such content of raw materials, the value of the strength limit is lower by 60-65%, which is due to the presence of excess moisture.

The lowest compressive strength values (15.3 MPa) have biocomposite materials whose composition content in the mould cavity was 11 g. The composition was not additionally compressed during the main heat treatment of the biocomposite in the mould (Figure 6.3). At the same time, the high content of the composition in the mould ensured a high density (Table 6.1) of the biocomposite material compared to the content of 9 g and 10 g of the composition for the same volume of the mould cavity.

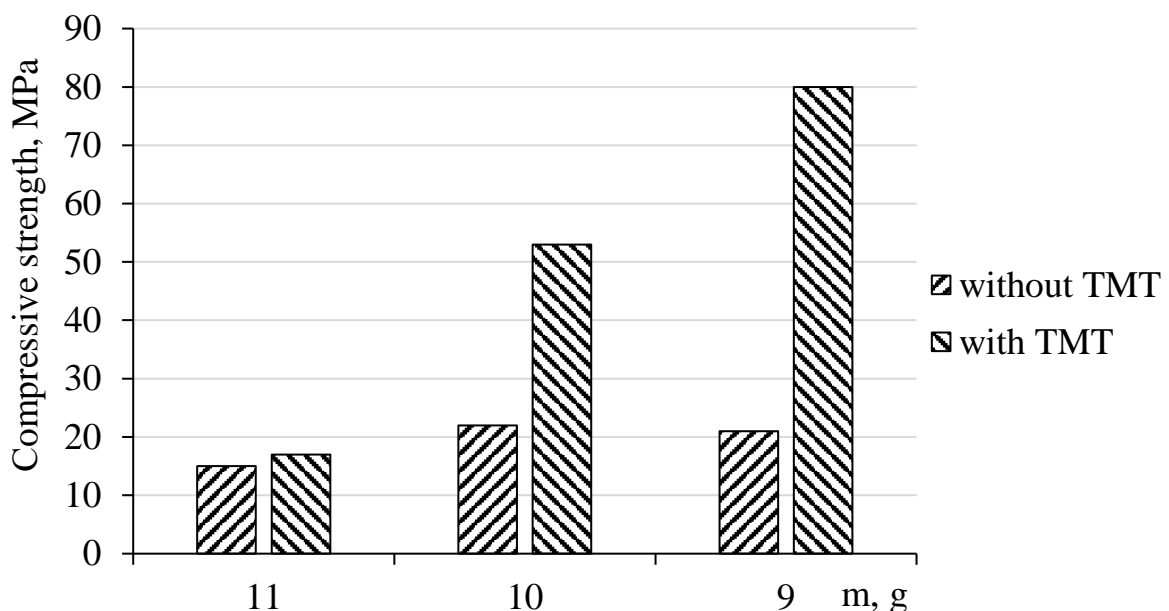


Figure 6.3. Dependence of compressive strength of biocomposites based on secondary raw materials (70%) on material density and thermo-mechanical treatment

The technological process of forming biocomposites involves thermo-mechanical processing, which consists of additional compression of the composition after exposure

to a thermal field for 1 hour, which provides an additional increase in the degree of compaction. Since the composition had a high density at the beginning of processing in the thermal field, additional compression was complicated, which resulted in almost no change in the volume of the sample and the density of the material. If a high density of the material is achieved during the main heat treatment, it becomes impossible to completely remove the water included in the gluten solution from the volume of the biocomposite material, which leads to the blocking of the formation of bonds between the components of the biocomposite.

Table 6.1.

Density distribution of biocomposites depending on thermo-mechanical treatment

Mass of the composition in the mould cavity, g	11	10	9
Density of biocomposite without TMT, g/cm ³	1,17	1,06	0,95
Density of biocomposite after TMT, g/cm ³	1,17	1,18	1,19

The use of a smaller amount of the composition (10 g) for the formation of a biocomposite sample without additional compression provided an increase in the compressive strength limit by 30%, which is associated with the possibility of moisture removal in a less dense structure. In the case of additional compaction of the composition, the compressive strength of biocomposites is 52.4 MPa, which is due to the removal of moisture at the first stage of heat treatment and additional compaction of the composition due to compression. This ensured the elimination of cavities that appeared as a result of moisture evaporation and the formation of additional physicochemical bonds between amino acid macromolecules and the surface of the filler.

In the case of using the content of the composition in the amount of 9 g, there is a significant removal of moisture, which leads to the formation of a porous structure of the material, which is unable to resist static compressive loads. As a result, there should be a significant decrease in the compressive strength limit, which does not occur due to the compensation of the formation of a more rigid framework of macromolecules of the biopolymer matrix.

The highest compressive strength values of biocomposites (79.8 MPa) were obtained due to additional compression, which made it possible to compact the composition in a thermal field. This ensures the removal of excess moisture and the transition of the biopolymer binder into a gel-like state, which is characterized by high manufacturability and fluidity, which determines the ability to move macromolecules, their compaction and the formation of additional connections between components.

Biocomposite materials have high compressive strength values after keeping the samples at room temperature for 5-7 days (Figure 6.4). In this case, the material gradually loses the remaining moisture, which is contained in the central part of the samples by diffusion movement of water molecules to the peripheral zone, followed by evaporation from the surface layer. In the case of a decrease in moisture, the biopolymer structure is compacted with an increase in the rigidity of the macromolecular framework and the formation of physicochemical bonds.

In order to intensify the moisture removal process, additional heat treatment was carried out at a temperature of 50 °C for 1 hour and 2 hours. As a result of this heat treatment, the compressive strength limit is slightly reduced by 3-5%, which is associated with the intensive removal of moisture from the surface layers, which become brittle, and the central part of the sample contains residual moisture, which ensures plasticity. Under the influence of a static compressive load, elastic deformation of the peripheral zone occurs, which is not able to fully resist destruction, since the central part is subjected to plastic deformation.

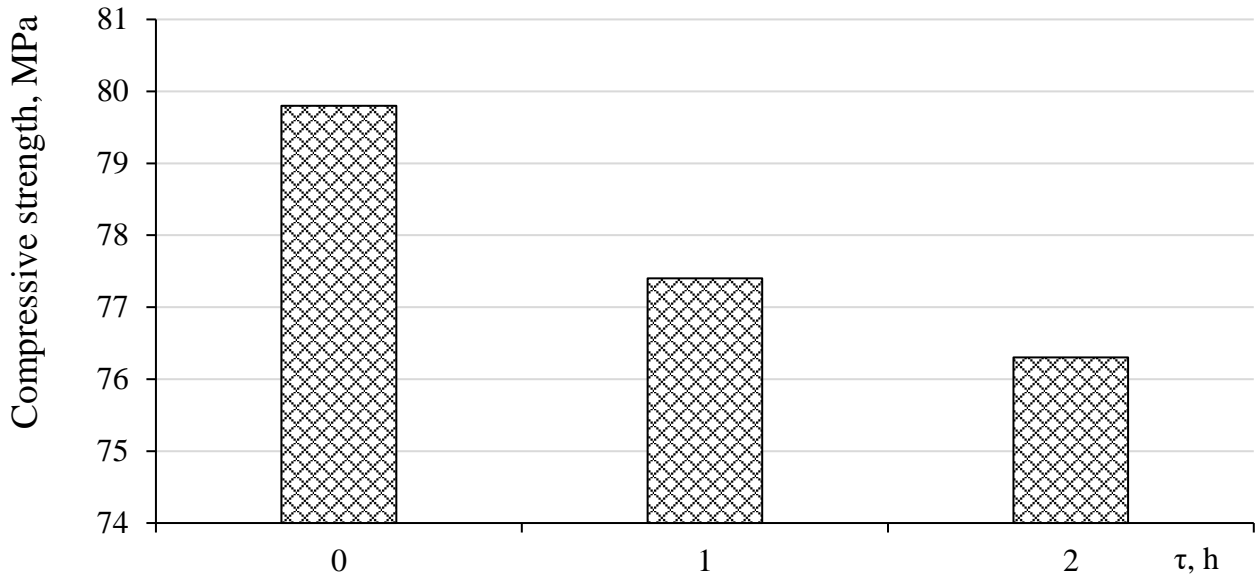


Figure 6.4. Dependence of the compressive strength of biocomposites on the duration of additional heat treatment at a temperature of 50 °C

Conclusions. The developed technology of recycling biocomposite products is a combined method that allows you to obtain secondary raw materials in the form of a powdered product that is saturated with amino acids of gluten. The resulting powder has high manufacturability, which ensures the formation of new biocomposite products with high operational characteristics.

Secondary raw materials have residual gluten content, which is not completely removed during combined processing in the recycling process, which affects the formation of new biocomposite materials. At the same time, the optimal content of the gluten solution in the composition should be reduced to 30% compared to the optimal content of 40% under the condition of using primary raw materials. This is due to the lower moisture content and the ability to form a rigid framework from the macromolecules of the biopolymer matrix.

The use of a low-density filling of the mould cavity with a biopolymer composition ensures the removal of water molecules from the cells of the glutinous binder and the transition of the system to a gel-like state, which leads to an increase in fluidity and a uniform distribution of amino acids. The expediency of carrying out an additional

compression operation after the transition of the biopolymer binder into a gel-like state, which ensures the formation of common groups with other groups of gluten macromolecules, the filling of cavities and the formation of a homogeneous structure of the biocomposite material, has been determined. As a result, a dense structure of biocomposite material with high compressive strength (78.9 MPa) is formed.

It is advisable to remove residual moisture under normal conditions, which allows you to preserve the structure of the biocomposite material without destroying the physical and chemical bonds and the appearance of areas with an increased stress state.

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