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STUDY OF THE STRUCTURE AND ADHESIVE PROPERTIES OF EPOXY COMPOSITES FILLED WITH BIOGENIC MICRODISPERSE FILLER

The work investigated the effect of organic biogenic lignocellulosic filler obtained from coffee production waste on the adhesive properties and residual stresses of epoxy composites. The relevance of this study stems from the growing interest in utilizing renewable secondary raw materials as functional additives for the development of polymeric materials. The adhesive strength at separation and residual stresses were determined using the ASTM separation method, and the mechanism of interfacial interaction was analyzed based on morphological analysis of the fracture surfaces. The polyfunctional nature of the filler was established by the method of IR spectroscopy, due to the presence of hydroxyl –OH ($\nu = 3425$ cm^{-1}), carbonyl C=O ($\nu = 1655$ cm^{-1}) and ether ($\nu = 1057$ cm^{-1}) C–O–C groups, which form a high density of polar centers. It has been established that the introduction of a filler in the amount of 0.50…1.00 wt.% into the epoxy binder ED-20 provides a synergistic effect of the interaction of the ingredients (hydrogen and dipole-dipole interactions), which leads to the transition of the failure mechanism from adhesive to cohesive. At the optimal filler content (0.50…1.00 wt.%), the adhesive strength increases from 24.4 MPa to 34.2 MPa, and the residual stresses decrease by half.

Keywords: *epoxy resin, coating, adhesive strength, IR-spectral analysis, residual stresses, adhesive failure pattern.*

Introduction. Today, one of the priority areas of development of materials science and engineering of polymer materials is the use of waste from the agro- and food industry as functional fillers for polymer matrices. This approach aligns with the principles of sustainable development and the circular economy, combining the use of secondary raw materials with the formation of multifunctional polymer composites, the properties of which can be purposefully tailored during their structure formation [1-4]. The use of organic biogenic fillers of plant origin (in particular, waste from grain processing, coffee, sugar, and oil industries) allows not only to reduce the environmental load on the environment, but also to purposefully modify the structure and operational characteristics of polymers due to interfacial interaction, changes in polymerization kinetics, and the formation of a strongly cross-linked structure of composites [4-8].

Problem Statement and Analysis of Recent Publications. Analysis of the works of scientists [3-6] allows us to state that the introduction of dispersed biogenic fillers into thermosetting polymer matrices, in particular epoxy resins, will enable us to increase the adhesive strength, wear resistance, heat resistance, and barrier characteristics, and also provide a reduction in the fragility of polymer materials [6-8]. At the same time, the effectiveness of the modification is determined by the chemical nature of the filler, its dispersion, specific surface area, and the presence of functional groups that are capable of physicochemical interactions with the polymer matrix. Thus, the use of agro- and food industry waste as functional additives is considered not only an environmentally sound solution but also a scientifically sound tool for regulating the properties of polymer composites in engineering applications.

The purpose of the work is to study the influence of the content of biogenic microdisperse filler on the properties of epoxy composites.

Materials and research methods. To create epoxy composites and coatings based on them, the following were used: binder – epoxy oligomer ED-20 (ISO 18280:2010); hardener – polyethylene polyamine, PEPA (TU 6-05-241-202-78).

To improve the properties of epoxy composites and coatings based on them, an organic biogenic lignocellulosic filler (OBLC) was used as a filler, obtained by grinding and fractionating coffee production waste (coffee grounds). The dispersion of the filler is 10-20 microns.

The choice of organic biogenic lignocellulosic filler (OBLC) is due to its chemical composition and functional properties. The main components of OBLC are cellulose (35–45%), hemicellulose (20–30%), and lignin (20–25%), which can form a rigid biopolymer framework in an epoxy matrix. The presence of a significant number of hydroxyl (–OH) groups in the structure of cellulose and hemicellulose provides an increase in the adhesive interaction at the interface of the phases "epoxy matrix – microdispersed filler" due to the formation of hydrogen bonds with polar epoxy and hydroxyl fragments of the polymer network. Lignin, as an aromatic polymer with enhanced thermal stability, contributes to increased stiffness in the composite and improved thermal and corrosion resistance. Additionally, extractive substances (lipids, phenolic compounds) are present, which can act as secondary modifiers, influencing the processes of structure formation and relaxation of residual stresses in the polymer matrix.

Thus, the use of OBLC as a filler for epoxy composites is scientifically justified and appropriate from the perspective of forming materials with controlled adhesion characteristics.

Epoxy composites were formed using the technology described in [9, 10].

The adhesion strength of the coatings upon separation was determined according to ASTM D897-08 [11].

The residual stresses of the polymer coating films were determined using the method described in [11].

The structure of the studied materials was analyzed using IR spectral analysis [10]. IR spectra were recorded on a spectrophotometer of the brand "IRAffinity-1" (Japan) in the wave number range $\nu = 500\ldots4000$ cm^{-1} by the single-beam method in reflected light. The IR-spectra were calculated using the IRSolution software.

Discussion of the results of the experiment. To substantiate the regularities of the influence of organic biogenic lignocellulosic filler (OBLC) on the adhesive strength at separation and residual stresses of epoxy composites, an IR spectral analysis of the additive (Fig. 1) was carried out in the wavenumber range $\nu = 500\ldots4000$ cm^{-1}. Based on the IR spectral analysis, functional groups (Table 1) that participate in the interfacial interactions of the system “epoxy matrix – filler” and “epoxy matrix – filler – metal substrate” were identified.

Therefore, based on IR-spectral analysis (Fig. 1, Table 1), it can be stated that OBLC is a polyfunctional organic filler, due to the presence in its structure of a complex of different types of polar functional groups (–OH, C=O, C–O–C, $–CH_2–$) with a high density of polar centers capable of active interfacial interaction with the epoxy oligomer ED-20. This enables us to make assumptions about the various mechanisms of interfacial interaction between ingredients during the polymerization process.

A comprehensive analysis of the results of the study of the adhesion strength at separation (Fig. 2), the morphology of the fracture surfaces (Fig. 3a-e), and the structure of the materials (IR-spectroscopy) allows us to analyze the adhesion mechanism in epoxy composites filled with organic biogenic lignocellulosic filler (OBLC).

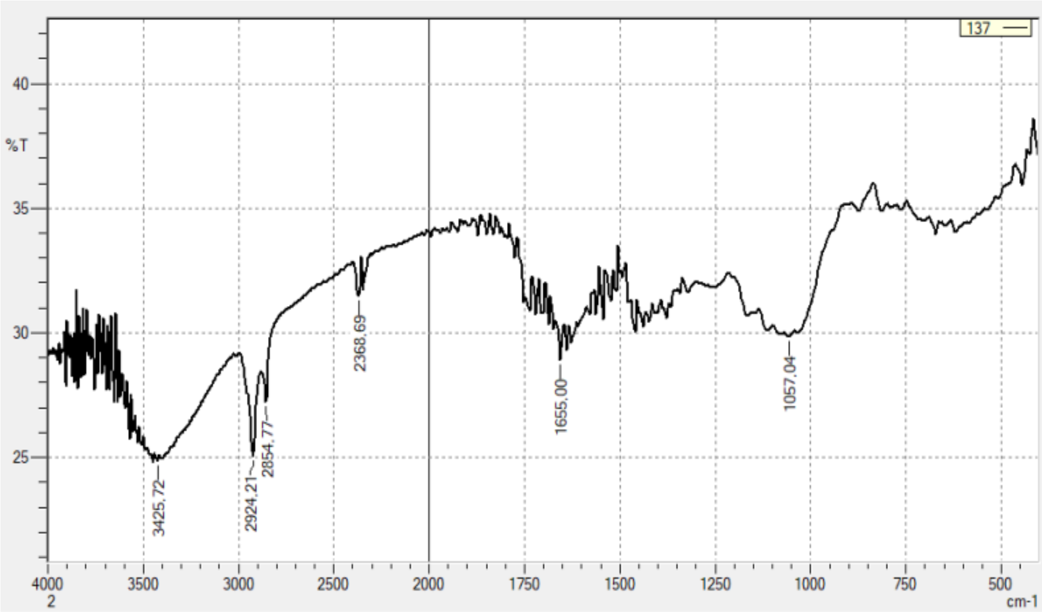


Fig. 1. IR spectrum of organic biogenic lignocellulosic filler in the wavenumber range $\nu = 500\ldots4000$ cm^{-1}.

Analysis of the curves of the dependences of the adhesion strength and residual stresses indicates the nonlinear, extreme nature of the influence of OBLC on the properties of the system "epoxy matrix - metal substrate".

For the unfilled epoxy matrix (Fig. 3a), the adhesive type of fracture prevails, as evidenced by a significant area where a clean metal surface is observed. Such morphological features of the separation surface indicate that there is limited interfacial interaction and the presence of increased residual stresses, which correlates with the values of σ_z (Fig. 2, curve 2).

Table 1.

IR-spectral analysis of biogenic lignocellulosic filler

Groups corresponding to characteristic absorption bands	Wave number, ν, cm^{-1}	Intensity, *T*, %	Relative peak area, *S*, %
Stretching vibrations of C–O–C and C–O groups, characteristic of the cellulose component (a key marker of the lignocellulosic nature of the filler)	1057	29.8	18.9
Vibrations of C=O groups (indicating carbonyl fragments in the filler structure)	1655	28.8	16.2
Oscillations characteristic of porous biogenic materials	1368	31.4	31.3
Stretching vibrations of $–CH_2–$ and $–CH_3–$ groups of aliphatic fragments characteristic of the hydrocarbon component of the filler	2854	27.2	20.8
	2924	25.0	81.1
Stretching vibrations of hydroxyl groups (–OH) characteristic of cellulose, hemicellulose, and phenolic fragments of lignin	3425	24.8	96.6

When introducing organic biogenic lignocellulosic filler at a content of $q = 0.50…1.50$ wt.% (Fig. 2b,c) a transition to the adhesive-cohesive and cohesive failure mechanisms was observed. The morphology of the separation surfaces is presented as being covered with a continuous layer of polymer, characterized by a microrough texture, which indicates failure in the volume of the adhesive, rather than along the polymer-metal phase interface. Such morphology is consistent with the maximum values of the adhesive strength, the values of which increase from $\sigma_a = 24.4$ MPa (unfilled epoxy matrix) to $\sigma_a = 25.2…34.2$ MPa and minimum residual stresses ($\sigma_a = 1.14…1.21$ MPa).

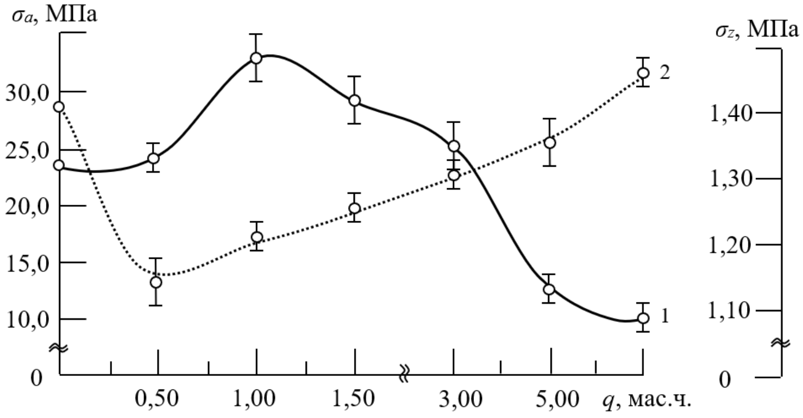
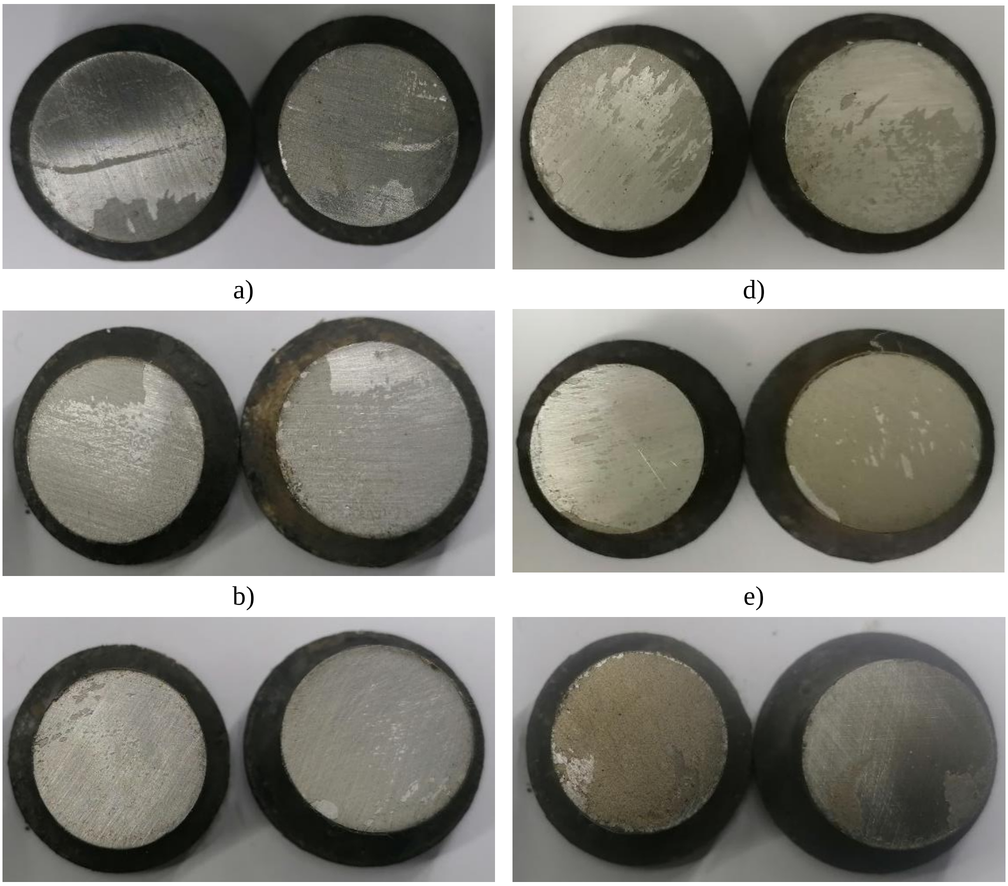


Fig. 2. The effect of the content of organic biogenic lignocellulosic filler (OBLC) on the adhesive strength at separation and residual stresses of epoxy composites:
1 – adhesive strength at separation (σ_a); 2 – residual stresses (σ_z).

From a materials science point of view, this is due to the synergistic action of physicochemical mechanisms, namely, the formation of an intense adhesive contact, which is realized due to hydrogen bonds between hydroxyl groups (–OH) of lignocellulosic components of OBLC ($\nu = 3425$ cm^{-1}) and polar groups of the epoxy matrix, i.e. epoxy fragments $–CH–CH_2–O–$ ($\nu = 915…920$ cm^{-1}) [12] and hydroxyl groups –OH ($\nu = 3500…3350$ cm^{-1}) [13-15], which arise as a result of the opening of epoxy rings during the polymerization process. Such an interaction mechanism increases the surface energy of the contact and contributes to the transition of the fracture nature from adhesive to cohesive. In addition, polysaccharide C–O–C fragments ($\nu = 1057$ cm^{-1}) contribute to the formation of an extended interfacial zone with increased cohesive strength. While carbonyl polar fragments ($\nu = 1655$ cm^{-1}) can participate in dipole-dipole interactions, stabilizing the structure in the surface layer of the polymer. The above assumption is based on the results of the study of IR-spectral analysis of the microdispersed filler (Fig. 1, Table 1), in particular: hydroxyl groups –OH ($\nu = 3425$ cm^{-1}), characteristic of cellulose, hemicellulose and phenolic fragments of lignin; carbonyl groups C=O ($\nu = 1655$ cm^{-1}), characteristic of lignin components; C–O–C fragments $\nu = 1057$cm^{-1}), characteristic of the cellulose component. The identified groups are characterized by an asymmetric distribution of electron density, which forms local electric dipoles.



a) d)

b) e)

c) f)

Fig. 3. Morphological features of the separation surface of epoxy adhesives with different contents of organic biogenic lignocellulosic filler (OBLC), q, wt.%:

a) epoxy matrix; b) 0.50; c) 1.00; d) 3.00; e) 5.00; f) 7.00.

While the epoxy oligomer ED-20 contains in its structure: epoxy rings –CH–CH_2–O–; hydroxyl groups –OH; ether bonds –C–O–C– in the polymer chain, which also have a significant dipole moment, which creates conditions for electrostatic interaction with the polar centers of the OBLC and the metal base. Thus, the dipole-dipole interaction occurs due to the orientational attraction between the permanent dipoles of the functional groups of the filler, matrix, and substrate. Therefore, the following types of interactions were assumed:

- between the dipole –OH (organic biogenic lignocellulosic filler) and the dipole C–O or –OH (epoxy matrix);
- between the C=O dipole (organic biogenic lignocellulosic filler) and polar fragments of the polymer network;
- between the C–O–C ether groups of both components.

As a result, the cohesive nature of the fracture is realized (Fig. 3b,c), which corresponds to the maximum value of the adhesive strength (σ_a = 34.2 MPa) and a 2-fold decrease in residual stresses (Fig. 2, curves 1, 2) at the polymer-substrate phase interface.

A further increase in the content of the organic biogenic lignocellulosic filler to q = 3.0…7.0 wt.% is accompanied by a significant change in the nature of the fracture. The separation surfaces are characterized by the presence of a heterogeneous coating (Fig. 3d-e). In this case, the presence of clearly defined point zones of the metal base indirectly indicates the agglomeration of the filler particles. This effect leads to the formation of local stress concentrators that initiate premature failure. As a result, we observed a decrease in adhesion strength and an increase in residual stresses with increasing filler content (Fig. 2, curves 1, 2).

Conclusion. Based on the comprehensive results of the study, the following was established:

1. The presence of polar functional groups –OH, C=O, C–O–C in the structure of the organic biogenic lignocellulosic filler was established by the method of IR-spectral analysis, which creates conditions for the implementation of dipole-dipole interaction with polar fragments of the epoxy matrix. Such interaction affects the course of the structure formation processes, which ensures improved wetting of the filler by the polymer, as well as a reduction of residual stresses at the interface between the phases of the system “polymer – filler” and “polymer – filler – metal substrate”.

2. The regularities of the influence of organic biogenic lignocellulosic filler on the formation of a polymer coating with increased values of adhesive strength have been established, where polysaccharide C–O–C fragments provide structural compaction of the adhesive film, and carbonyl C=O groups stabilize the surface layer of the polymer film due to dipole-dipole interaction. In this case, the transition of the fracture mechanism from adhesive to cohesive is realized at a certain filler content (q = 1.00 wt. %), which is confirmed by the morphology of the separation surfaces and is accompanied by an increase in the value of adhesive strength from σ_a = 24.4 MPa to

$\sigma_a = 34.2$ MPa and a decrease in residual stresses from $\sigma_z = 1.40$ MPa to $\sigma_z = 1.14…1.21$ MPa.

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ДОСЛІДЖЕННЯ СТРУКТУРИ І АДГЕЗІЙНИХ ВЛАСТИВОСТЕЙ ЕПОКСИДНИХ КОМПОЗИТІВ, НАПОВНЕНИХ БІОГЕННИМ МІКРОДИСПЕРНИМ НАПОВНЮВАЧЕМ

У роботі досліджено вплив органічного біогенного лігноцелюлозного наповнювача, отриманого з відходів кавового виробництва, на адгезійні властивості та залишкові напруження епоксидних композитів. Актуальність дослідження зумовлена зростаючим інтересом до використання відновлюваної вторинної сировини як функціональних добавок для створення полімерних матеріалів. Адгезійну міцність при відриві та залишкові напруження визначали методом відриву згідно ASTM, а механізм міжфазової взаємодії аналізували на основі морфологічного аналізу поверхонь руйнування. Методом ІЧ-спектроскопії встановлено поліфункціональну природу наповнювача, обумовлену наявністю гідроксильних –OH ($\nu = 3425$ см$^{-1}$), карбонільних C=O ($\nu = 1655$ см$^{-1}$) та ефірних ($\nu = 1057$ см$^{-1}$) C–O–C груп, що формують високу густину полярних центрів. Встановлено, що введення у епоксидний зв'язувач ЕД-20 наповнювача у кількості 0,50…1,00 мас.ч. забезпечує синергетичний ефект взаємодії інгредієнтів (водневих та дипольно-дипольних взаємодій), що приводить до переходу механізму руйнування з адгезійного в когезійний. За оптимального вмісту наповнювача (0,50…1,00 мас.ч.) адгезійна міцність підвищується з 24,4 МПа до 34,2 МПа, а залишкові напруження знижуються у два рази.

Ключові слова: епоксидна смола, покриття, адгезійна міцність, ІЧ-спектральний аналіз, залишкові напруження, характер руйнування адгезиву.

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