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ДОСЛІДЖЕННЯ СТРУКТУРИ ЕПОКСИДНИХ КОМПОЗИТІВ МЕТОДОМ ОПТИЧНОЇ МІКРОСКОПІЇ ТА ІЧ-СПЕКТРАЛЬНОГО АНАЛІЗУ

Для формування полімерних матеріалів використано епоксидний діановий оліґомер ЕД-20, полімеризацію якого виконували за допомогою амінного твердника поліетиленполіаміну ПЕПА. Підвищення властивостей епоксидних композитів досягали шляхом використання суміші дискретних волокон на основі поліестеру, віскози, еластану, вміст яких змінювали у межах q = 0,25…2,00 мас.%. У роботі досліджували характер руйнування поверхні епоксидних композитів методом оптичної мікроскопії, що дозволив визначити особливості взаємодії інгредієнтів і стійкість розроблених матеріалів до впливу навантажень ударного характеру. Додатково досліджували міжфазову взаємодію інгредієнтів композиту з використанням методу ІЧ-спектрального аналізу. Встановлено зміну параметрів інтенсивності (T, %), відносної площі піку (S, %), а також незначні зміщення хвильових чисел ($\Delta\nu$, см$^{-1}$), що відповідає коливанням груп: -NH-, O-H ($\nu = 3408$ см$^{-1}$), C-H, ($\nu = 2922…2848$ см$^{-1}$), C=O ($\nu = 2019$ см$^{-1}$), поліестерної складової ($\nu = 1700$ см$^{-1}$), C–O–C ($\nu = 1112…914$ см$^{-1}$) та вказує на структурні перетворення при полімеризації інгредієнтів композиту.

Ключові слова: *епоксидний олігомер ЕД-20, твердник ПЕПА, суміш дискретних волокон, оптична мікроскопія, ІЧ-спектральний аналіз.*

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RESEARCH OF THE STRUCTURE OF EPOXY COMPOSITES BY OPTICAL MICROSCOPY AND IR-SPECTRAL ANALYSIS

For the formation of polymer materials, the epoxy dian oligomer ED-20 was used, and its polymerization was performed using the amine hardener polyethylenepolyamine PEPA. The properties of epoxy composites were improved by using a mixture of discrete fibers based on polyester, viscose, and elastane, the content of which was varied within q = 0.25…2.00 wt.%. In this work, the nature of surface destruction in epoxy composites was investigated using optical microscopy, which enabled us to determine the interaction features between ingredients and the resistance of the developed materials to shock loads. Additionally, the interfacial interaction of the composite ingredients was investigated using the IR spectral analysis method. A change in the intensity parameters (T, %), relative peak area (S, %), as well as insignificant shifts in wave numbers ($\Delta\nu$, cm^{-1}) was established, which corresponds to vibrations of the groups: -NH-, O-H ($\nu = 3408$ cm^{-1}), C-H, ($\nu = 2922…2848$ cm^{-1}), C=O ($\nu = 2019$ cm^{-1}), polyester component ($\nu = 1700$ cm^{-1}), C–O–C ($\nu = 1112…914$ cm^{-1}) and indicates structural transformations during polymerization of the composite ingredients.

Keywords: *epoxy oligomer ED-20, hardener PEPA, mixture of discrete fibers, optical microscopy, IR spectral analysis*

Problem statement. Today, there is an urgent need to improve the performance characteristics of composite materials (CM), which is due to a set of industry requirements (reliability, product weight, manufacturing processability, durability, and a set of improved characteristics). That is why the study of new approaches to modifying polymer materials and improving the interfacial interaction of ingredients is a priority direction in performing materials science research. It should be noted that the introduction of active fibrous fillers into the polymer binder affects the course of physicochemical processes during crosslinking of epoxy composites [1]. In this case, the choice of fillers should take into account their chemical activity, i.e., the presence of active groups on the surface and in the structure capable of interacting with the epoxy and amine groups of the binder. Such an approach enables you to influence the kinetics of physicochemical processes in the polymerization of epoxy composites, the deformation mobility of the main chain and its segments, their ordering, and the formation of additional intermolecular bonds. At the same time, standardized methods for studying the properties of polymers do not always allow us to determine the regularities of structural transformations in polymers. Therefore, the use of precision methods for analyzing the structure, in particular optical microscopy and IR spectroscopy [2-4], is relevant. Such research methods aim to determine both the morphological features of polymer composites and the degree of their crosslinking, which enables us to influence the properties of these materials.

Analysis of recent studies and publications. The analysis of the authors' work [5] allows us to state that filling the epoxy matrix with discrete carbon fibers contributes to the reduction of thermal stresses in composites during operation at elevated temperatures. Such an effect is associated with the difference in the thermal coefficient of linear expansion between individual reinforcing components, which reduces the risk of local stress concentration zones in the matrix. The analysis of the authors' work [6] enables us to conclude that nitron fibers are effectively used for reinforcing the polymer matrix. Based on IR spectral analysis and optical microscopy, the authors proved the interfacial interaction of the ingredients. Such an effect is due to the absence of an absorption band in the filled polymer, which is responsible for the hydroxyl (-OH) groups at a vibration frequency of v = 3450 cm-1. This indicates the intermolecular interaction of the ingredients used, and therefore, high mechanical characteristics. Thus, based on the analysis of scientific works [6-10], it can be stated that the combination of modern methods for studying the structure of epoxy composites filled with fibrous additives allows us to localize areas of weakened adhesion and fiber aggregation, and prevent similar anomalous morphological and chemical changes in the polymer volume.

The purpose of the work is to study the inter-vessel interaction of ingredients during the structure formation of epoxy composites.

Materials and research methods. As the main component for the formation of epoxy composites, epoxy resin of the ED-20 brand (ISO 18280:2010) was used.

For the polymerization of epoxy composites, the hardener polyethylene polyamine PEPA (TU 6-05-241-202-78) was used, which is characterized by the presence of amine groups as reaction centers, allowing for curing of polymers at room temperature.

As a filler, a mixture of discrete fibers (MDFOOPVE) of organic origin based on polyester (75%), viscose (23%), elastane (2%) with the following parameters was used: $l = 15…30$ μm, $d = 15…20$ μm.

Epoxy composites were formed according to the technology described in the work [7].

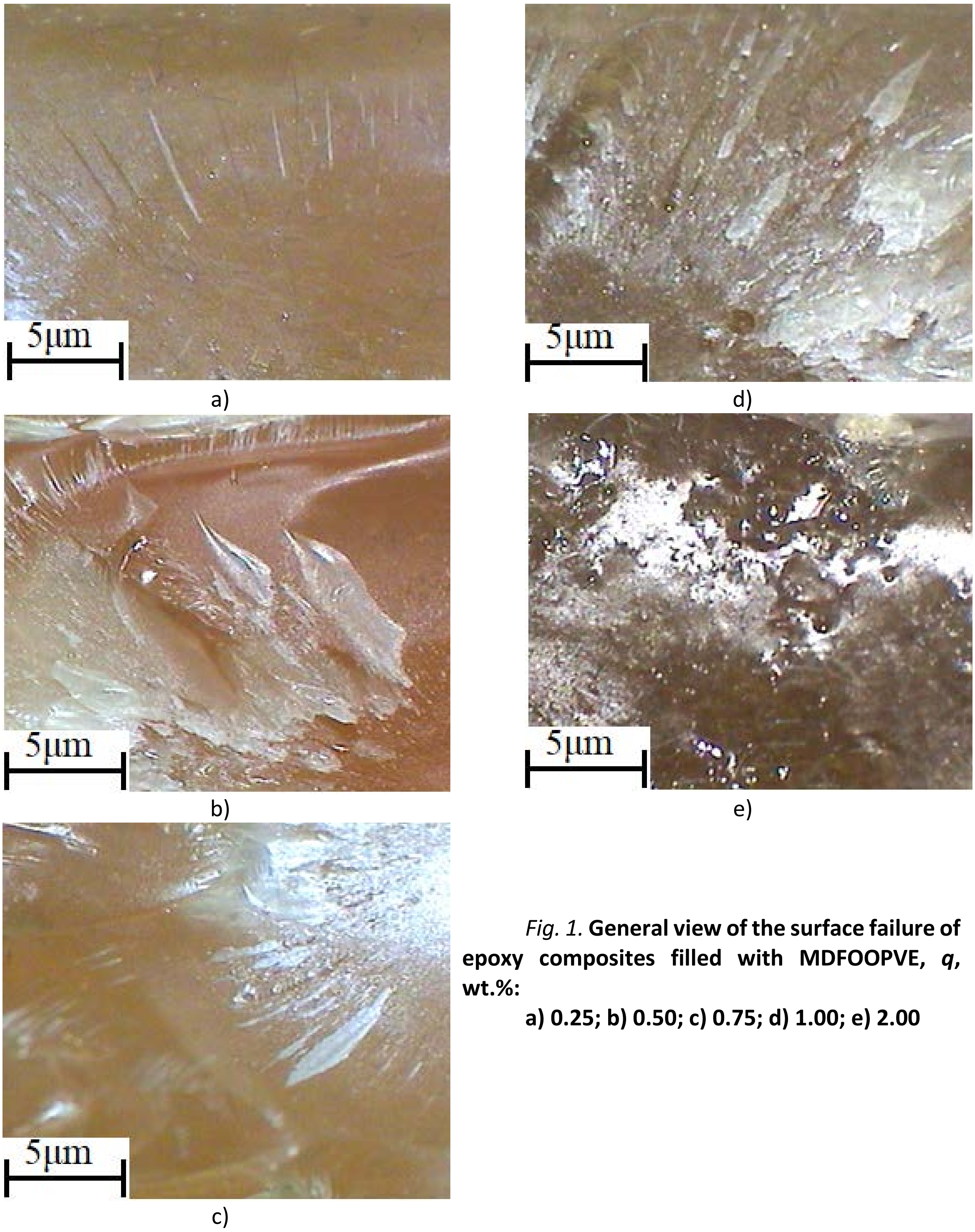
The study of the composite structure was conducted using a microscope model XJL-17AT. For digital image processing, the software "Levenhuk Toup View" was used.

To study chemical bonds and their changes in the epoxy composite, IR spectral analysis was used [2, 4]. IR spectra were recorded on a spectrophotometer of the brand "IRAffinity-1" (Japan) in the wavenumber range $\nu = 400…4000$ cm^{-1} by the single-beam method in reflected light.

Discussion of the results. Based on the previous results of the study [7] of the influence of a mixture of discrete fibers (MDFOOPVE) on the properties of epoxy composites, an increase in their characteristics was established at the additive content $q = 0.50…0.75$ wt.% (compared to an unfilled epoxy matrix). In particular, an increase in the value of the destructive stresses during bending from $\sigma_b = 48.0$ MPa to $\sigma_b = 74.0…90$ MPa, the modulus of elasticity during bending from $E = 2.7$ GPa to $E = 3.1…3.4$ GPa, and the impact strength from $W = 7.0$ kJ/m^2 to $W = 10.0…12.8$ kJ/m^2 was observed. A similar effect of the mixture of discrete fibers was also found in the study of thermophysical properties, in particular, an increase in the Martens heat resistance from $T = 341$ K to $T = 343$-344 K and a decrease in the thermal coefficient of linear expansion (TCLE), respectively, were observed. To analyze morphological changes in the material structure, a microscope model XJL-17AT with the software "Levenhuk Toup View" was used. The nature of the fracture in epoxy composites, as determined by TCLR and impact toughness studies, was investigated. Thus, the method of optical microscopy established the localized distribution of microcracks within the polymer volume (Fig. 1a). The nature of the fracture of the epoxy composite filled with $q = 0.25$ wt.% of MDFOOPVE indicates moderate adhesion between the fibrous filler and the polymer matrix.

In contrast, the formation of microcracks in the direction of the applied load was observed. Based on the obtained fracture images, the polymer's structure is relatively plastic, characteristic of a low level of reinforcement. When introducing MDFOOPVE at a content of $q = 0.50$ wt.% into the epoxy oligomer ED-20, a combined fracture mechanism was observed (Fig. 1b). That is, signs of quasi-brittle behavior with the formation of large fragments and plastic crushing of the polymer matrix are simultaneously detected. In this case, the surface of the composite material exhibits pronounced wavy shear zones, which alter the trajectory of crack propagation and are accompanied by the dissipation of impact energy within the polymer volume. This indicates increased interphase interaction, which provides high-strength indicators. A somewhat different nature of fracture was observed when $q = 0.75$ wt.% of MDFOOPVE was introduced. The polymer surface is characterized by a pronounced quasi-brittle nature of fracture (Fig. 1c), where the propagation of the crack network occurs through cells of increased rigidity. An increase in the MDFOOPVE content ($q = 1.00…2.00$ wt.%) ensures the formation of a defective polymer structure. For example, a KM filled with $q = 1.00$ wt.%. MDFOOPVE is characterized by the most brittle type of fracture, where large fragments and a significant number of cracks with slight air inclusions prevail (Fig. 1d). Such morphological defects indicate oversaturation of the matrix with fibers, which changes the mechanics of load transfer. Analysis of the fracture surface of CM filled with $q = 2.00$ wt.% of MDFOOPVE enabled us to identify brittle fracture centers characterized by the formation of a significant number of microcracks and stress concentrators, as indicated by traces of air inclusions (Fig.1e). This nature of the fracture of the polymer surface indicates an excess content of fibers, which reduces the efficiency of their interaction with the matrix and contributes to the rapid propagation of cracks.

Additionally, the chemical interaction of the CM ingredients was determined by IR spectral analysis (Fig. 2). The absorption bands of composites filled with $q = 0.25$-0.50wt.% of MDFOOPVE were analyzed in the wave number range $\nu = 400\ldots4000\ \text{cm}^{-1}$ (Table 1). The IR-spectral analysis method established the presence of a broad spectrum of absorption bands that characterize the valence, pendulum, and deformation vibrations of the side groups and segments of CM.



a) d)

b) e)

c)

Fig. 1. **General view of the surface failure of epoxy composites filled with MDFOOPVE, *q*, wt.%:**

a) 0.25; b) 0.50; c) 0.75; d) 1.00; e) 2.00

Analysis of IR spectra enabled us to detect structural changes, specifically a shift in frequency (ν, cm^{-1}), a change in transmission intensity (*T, %*), and a change in relative peak area (*S, %*). This indicates a different number of chemical bonds in the polymer, and, consequently, a change in the degree of crosslinking of the developed composites. Analysis of IR spectra (Fig.2a-c) allowed us to detect absorption bands characteristic of the hydroxyl group OH ($\nu = 3408\ \text{cm}^{-1}$) for composites containing $q = 0.25$-0.50 wt.% of MDFOOPVE.

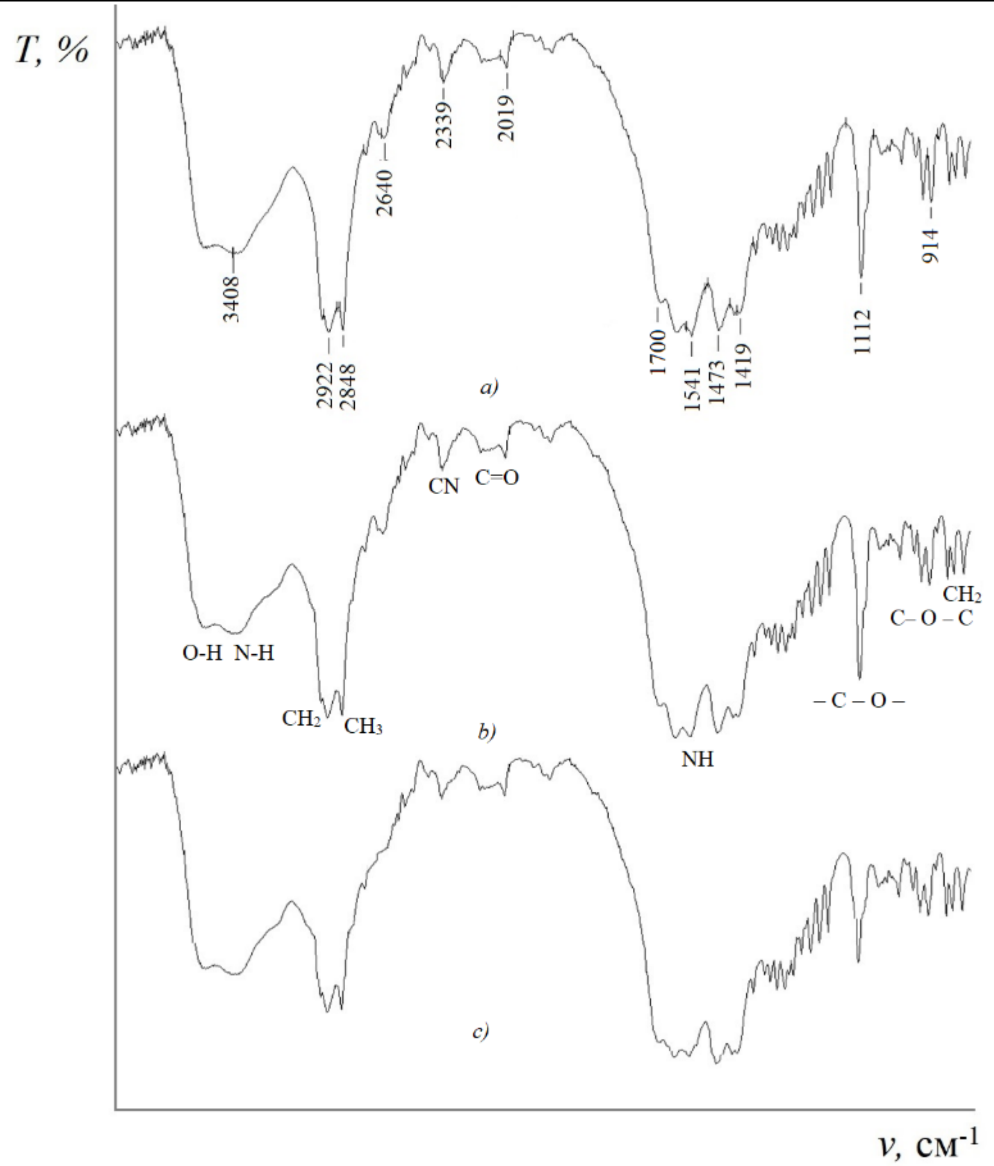


Fig. 2. **IR spectra of composite materials in the wavenumber range ν = 400…4000 cm^{-1}: a – 0.25 wt.% of MDFOOPVE; b – 0.50 wt.% of MDFOOPVE; c – 0.75 wt.% of MDFOOPVE**

At the same time, a shift of the peak towards lower frequencies and a change in the relative area of the peaks were observed. The maximum shift of the peak towards lower frequencies ($\Delta\nu$ = 3.86 cm^{-1}) was observed for CM containing q = 0.75 wt.% of MDFOOPVE. Such materials are characterized by the smallest value of the relative peak area – S = 88.1 % (Table 1). This indirectly indicates the formation or strengthening of hydrogen bonds between the hydroxyl groups of viscose and the polar groups of the epoxy matrix. The absorption bands at the wave number ν = 2922 cm^{-1} were attributed to asymmetric/symmetric CH_2 groups, and at ν = 2848 cm^{-1} – to asymmetric/symmetric CH_3, characteristic of all components of the mixture of discrete fibers (polyester, viscose, elastane). The increase in the intensity of the absorption bands (*T, %*) with increasing MDFOOPVE content (Table 1) indicates an increase in the proportion of organic fibers in the composition, confirming their presence in the polymer structure. The presence of a peak at ν = 2640 cm^{-1} is characteristic of overtrons of other groups. That is, these are bands that arise not from vibrations, but from multiple energy transitions in molecular groups during valence stretching.

The absorption band at ν = 1700 cm^{-1} is characteristic of the polyester component C=O (ester, polyester). While the range of wave numbers ν = 1419…1541 cm^{-1} indicates deformation vibrations of CH_2/CH_3 groups, which are due to an increase in the additive content. The absorption band at ν = 1112 cm^{-1} indicates ether bridges of epoxy groups and ether bonds of polyester, which are indicators of fibers adsorbed by the polymer and affect the interfacial interaction. Changes in the relative area of the peak at ν = 914 cm^{-1} (Table 1) indicate the interaction of epoxy groups (C–O–C) during polymerization with a mixture of discrete fibers.

Table 1.

Characteristic absorption bands according to IR-spectral analysis of composites filled with MDFOOPVE

Характеристики смуги		ІЧ-спектри композитів					
		0,25 мас.ч.		0,50 мас.ч.		0,75 мас.ч.	
Група	ν, см$^{-1}$	T, %	S, %	T, %	S, %	T, %	S, %
Коливання епоксидних груп C–O–C	914	17,8	25,4	17,9	20,1	18,2	17,5
				Зміщення → $\Delta\nu$ = 3,86 см$^{-1}$		Зміщення → $\Delta\nu$ = 3,86 см$^{-1}$	
C–O–C, – C–O – Характерні для ефірів/ефірні містки поліестеру і епоксидних груп	1112	13,8	54,1	13,8	54,1	14,1	49,8
Деформаційні коливання N–H, CH_2, CH_3 груп Характерні для еластану/твердника	1419	11,0	15,4	11,2	15,0	11,4	14,9
	1473	11,2	17,3	11,2	17,3	11,8	17,0
	1541	11,1	16,1	11,2	16,0	11,3	15,9
C=O (ester, poliester) Характерні для поліестерної складової	1700	12,1	11,3	12,1	11,3	12,6	19,8
Карбонільна група C=O	2019	21,6	16,0	21,6	16,0	21,6	16,0
-CN- валентні коливання	2339	24,9	36,3	24,9	36,3	25,2	35,1
Овертрони інших груп	2640	19,9	17,1	20,0	16,9	-	-
Асиметричні та симетричні коливання зв'язків C–H аліфатичних груп (CH_2, CH_3)	2848	11,1	54,2	11,9	50,1	12,6	48,3
	2922	11,1	58,2	11,8	55,2	11,9	53,1
Валентні коливання O–H N–H груп	3408	13,6	98,9	14,2	90,2	15,6	88,1
				Зміщення → $\Delta\nu$ = 1,1 см$^{-1}$		Зміщення → $\Delta\nu$ = 3,86 см$^{-1}$	

Therefore, there are structural changes in the studied CM. It was established that for the composite filled with q = 0.25 wt.% of MDFOOPVE, the maximum relative peak area (S = 25.4%) was observed at ν = 914 cm^{-1}, which indicates a lower degree of conversion of epoxy groups compared to composites filled with q = 0.50-0.75 wt.% of MDFOOPVE. Additionally, the maximum value of the relative peak area (S = 98.6%) was observed at ν = 3408 cm^{-1}, indicating an insignificant interfacial interaction between the hydroxyl groups of viscose and the polar groups of the epoxy matrix. Then, as the decrease in the relative area of the peaks at ν = 3408 cm^{-1}, the weakening of the epoxy peak at ν = 914 cm^{-1} is an indicator of improved interaction of discrete fibers with the matrix, which is typical for CM filled with MDFOOPVE at a content of q = 0.50-0.75 wt.%.

Conclusions. The work compares the results of a study on the physical and mechanical properties and structure of epoxy composite materials filled with a mixture of discrete fibers based on polyester, viscose, and elastane. The work substantiates the possibility of controlled mechanical modification of the epoxy binder by introducing the optimal amount of a mixture of discrete fibers, which ensures improvement of the characteristics of epoxy composites. Additionally, generalized conclusions are made:

1. By optical microscopy, it was established that composites filled with q = 0.50–0.75 wt.% of MDFOOPVE are characterized by a combined fracture mechanism, which involves both localization and redirection of cracks in the polymer network, and therefore indicates effective interfacial interaction of the ingredients. Due to the nature of this fracture, the developed materials exhibit improved mechanical properties compared to other CMs studied in this work.

2. Based on IR-spectral analysis, it was found that when introducing a mixture of discrete fibers based on polyester, viscose, and elastane with a content of q = 0.50-0.75 wt.%, a decrease in the relative peak area from S = 98.9% to S = 88.1% at ν = 3408 cm^{-1} was observed and at the same time a decrease in the relative peak area from S = 25.4% to S = 17.5% at ν = 914 cm^{-1}. The results obtained can be interpreted as confirmation of intensive hydrogen interactions between the hydroxyl groups of viscose and the polar groups of the epoxy matrix, as well as an indicator of the reactive interaction of the ingredients. In parallel, an increase in the intensity of the absorption bands at ν = 1700 cm^{-1} and ν = 1112 cm^{-1} was observed, which characterizes the double and single bonds of the C=O and C–O groups, respectively, and indicates the participation of the polyester component in the interfacial interaction.

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