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Investigation of the phenomena revealed on phase interface in epoxide-composites

Summary: *The main task in the formation of epoxy material composites is to ensure optimal conditions for the physic-chemical interactions at the interface of oligomer - filler. Between the phases of the layers formed around dispersed particles of the filler appear zones possessing physical and mechanical properties different from other areas of composite material, formed during hardening. It is established that the geometric parameters of the interface layers, their interaction and the interaction with the filler cause significant changes in mechanical properties of epoxy composites, the instantaneous modulus during hardening in particular. The method of the outer surface layers images is carried out using the mathematical transformations and determination of the boundaries of the spatial clusters in the presence of dispersed filler particles. Boundaries of external surface layer around the particles of the dispersed filler is a blurred object and its metric parameters are not precise numbers. Based on the studies of metric characteristics of digital information of the outer surface layers of the epoxy composites thin films with dispersed fillers and the study of the theory of fuzzy sets the principles of application of the protective coating have been developed.*

Keywords: *composites, epoxy matrix, surface layers, optical methods*

BADANIA ZJAWISK NA GRANICY FAZ W KOMPOZYTOWYCH MATERIAŁACH EPOKSYDOWYCH

Streszczenie: *Głównym zadaniem podczas wytwarzania kompozytowych materiałów epoksydowych jest zapewnienie optymalnych warunków dla fizyczno-chemicznych oddziaływań na granicy faz oligomer - napełniacz. Pomiędzy fazami warstw wykształconych wokół rozproszonych cząstek napełniacza powstają strefy posiadające właściwości fizyczne i mechaniczne odmienne od innych obszarów materiału kompozytowego, powstałego podczas procesu sieciowania. Stwierdzono, że parametry geometryczne warstw międzyfazowych, ich wzajemne oddziaływanie i interakcja z napełniaczem powodują istotne zmiany właściwości mechanicznych kompozytów epoksydowych. Metoda obrazów zewnętrznych warstw powierzchniowych wykorzystuje matematyczne przekształcenia i określenia granic przestrzennych klastrów w obecności rozproszonych cząstek napełniacza. Granice zewnętrznej warstwy powierzchniowej wokół cząstek zdyspergowanego napełniacza jest niewyraźna, a jej metryczne właściwości nie są dokładnie określone. Opierając się na badaniach cech metrycznych uzyskanych na podstawie cyfrowej informacji dotyczącej zewnętrznej powierzchni warstw cienkich wytworów epoksydowych z rozproszonym napełniaczem i teorii zbiorów rozmytych zostały opracowane zasady stosowania powłoki ochronnej.*

Slowa kluczowe: *kompozyty, matryca epoksydowa, warstwy powierzchniowe, metody optyczne*

1. INTRODUCTION

Modern development of production requires the decrease of mechanisms and machines power – and metal consumption. Application of polymer composite materials is very promising. Epoxide polymers are of paramount importance. They possess good specific properties, technological effectiveness while forming coatings on the complex profile long-length surfaces, have well-developed raw material basis.

Creation of composite materials deals with the investigation of interaction on the boundary between the filler and polymer. Properties of materials, forming technology and the choice of fillers are not studied enough. Interaction on the interface in the composite using different as to their nature fillings at the stage of composite formation has not been investigated. Further improvement of the epoxide-composites characteristics were obtained undergoing them by the external energy fields: ultraviolet irradiation and ultrasound treatment.

In this case, transition zones of inter-phase interaction are formed on the interface between the filler and the binder. Properties of material of these zones differ from those of the matrix properties [1–3]. Investigations of these zone characteristics are described in this work by parameters of the external surface layers (ESL). In the works by Y. Lipatov composite materials are treated as the system of filler and external layers. Prof. G. Bartenief proposes to treat the formation of the polymer lattice as the development of the system of connected knots-clusters [4–5].

2. DESCRIPTION OF RESEARCH

The degree of binding in the external surface layers influences sufficiently the physical-mechanical properties composite materials determines their operational properties. Investigation of ESL parameters will make possible to propose new technologies of forming materials and coatings with high operation characteristics. The main parameters while developing new composite materials are: amount of the epoxide binder material contained in ESL.

The aim of the work is to find regularities of the influence of the composite forming technology or the main kinetics regularities of forming external surface layers structure, their geometric sizes and the degree of binding in them.

3. THE MATERIALS USED IN THE STUDY

ED-20 epoxide resin, hardener (PEPA) and fiber filler are investigated in the work (Table 1 and 2).

Table 1. Characteristics of the epoxide binder components
Tabela 1. Charakterystyka składników żywicy epoksydowej

Characteristics	Epoxide oligomer ED-20	Hardener PEPA
Molecular weight	390-430	230-250
Epoxide groups content, %	20,0-22,5	–
Hydroxide group content, %	1,25	–
Average function effectiveness according to epoxide groups, f_n	2,0	–
Viscosity η, Pa·s	13-20	0,9
Density ϱ, kg/m^3	1160	1050

Table 2. Physical-mechanical properties of fiber fillers
Tabela 2. Fizyczno-mechaniczne właściwości napełniacza włóknistego

Filler material	Density, ρ, kg/m^3	Ultimate compression strength, MPa	Modulus of elasticity, E, GPa	Specific surface, m^2/g	TCLE[*], $K^{-1}\times10^{-6}$
Ferrite	4650	300	45–215	15,3	-
Copper oxide	6400	1350	540	11,4	4,6
Aluminium oxide	3400-4000	55,2-344,8	103-358	18,4	5,5-8,0
BS (brown slame)	5120-5240	-	310,3	10–34	8,0-8,4
Boron carbide	2540	1840	380-490	12,1	4,5
Silicon carbide	3220	1030	103-358	7,2	4,7
CB (carbon black)	1900-2040	-	-	10-1000	2-3

[*]Thermal coefficient of linear expansion

The chosen fiber fillers are widely used in industry (Table 3). Basalt fiber is used as it possesses improved interaction with the epoxide matrix. Conventional methods of investigation as well as those developed at the Ternopil Ivan Puluj National Technical University have been used for these investigations [6]. The investigations were performed in some sequence stages: investigations of ESL, their structure, peculiarities of their forming and their influence on the physical-mechanical and operation characteristics of composites.

Table 3. Properties of fiber fillers
Tabela 3. Właściwości włókien napełniacza

Characteristics	Glass fiber	Basalt fiber	Carbon fiber
Density, kg/m^3	2500	1700	1800–2000
Melting temperature, K	1570–1920	1520	3920
Fiber diameter, μm	10–12	9–11	9–12
Tensile strength, MPa	2200–2600	2200–2800	1960–2960
Strength, %			
at 473 K	100	100	100
at 673 K	50	80	–
at 973 K	-	50	-
Modulus of elasticity, GPa	64–73	71–90	196–296
Water absorption, %	0,20	0,01	0,33

It is known that the process of epoxide-composite materials polymerization is accompanied by both fracture and activation of epoxide groups, increasing of the number of hydroxide ones, as well as revealing of small number of carbon groups in the outgoing oligomer. Taking advantage of the infrared-spectroscopy the interaction between the neigh-boring chains of macromolecules has been found. Using of the Langmure and Polyani adsorption models makes possible to determine possible mechanical of the interphase interaction between the macromolecules of the epoxide binder with the active centers on the surface of the dispersion particles of different physical nature [7, 8]. While investigating and decording of specimens infrared-spectrum chemical composition of the epoxide oligomer ED-20 molecules and PEPA hardener has been taken into account.

While investigating of gel-sol fraction it was found, that introduction of the dispersion particles of different physical nature in the epoxide binder with the content of 10–40 mass per cent per 100 mass per cent of the oligomer results in the increase of the gel-fraction in the matrix by 2–6%. Increase of the dispersion particles content more than 50 mass per cent does not result in the increase of matrix gelling degree, or, on the contrary, results in its decrease.

3. RESULTS OF RESEARCH AND DISCUSSION

The result of investigations made possible to conclude, that increase of the degree of the epoxide matrix binding can be obtained by regulation diffusion and relaxing processes while its structure forming. It is the degree of the

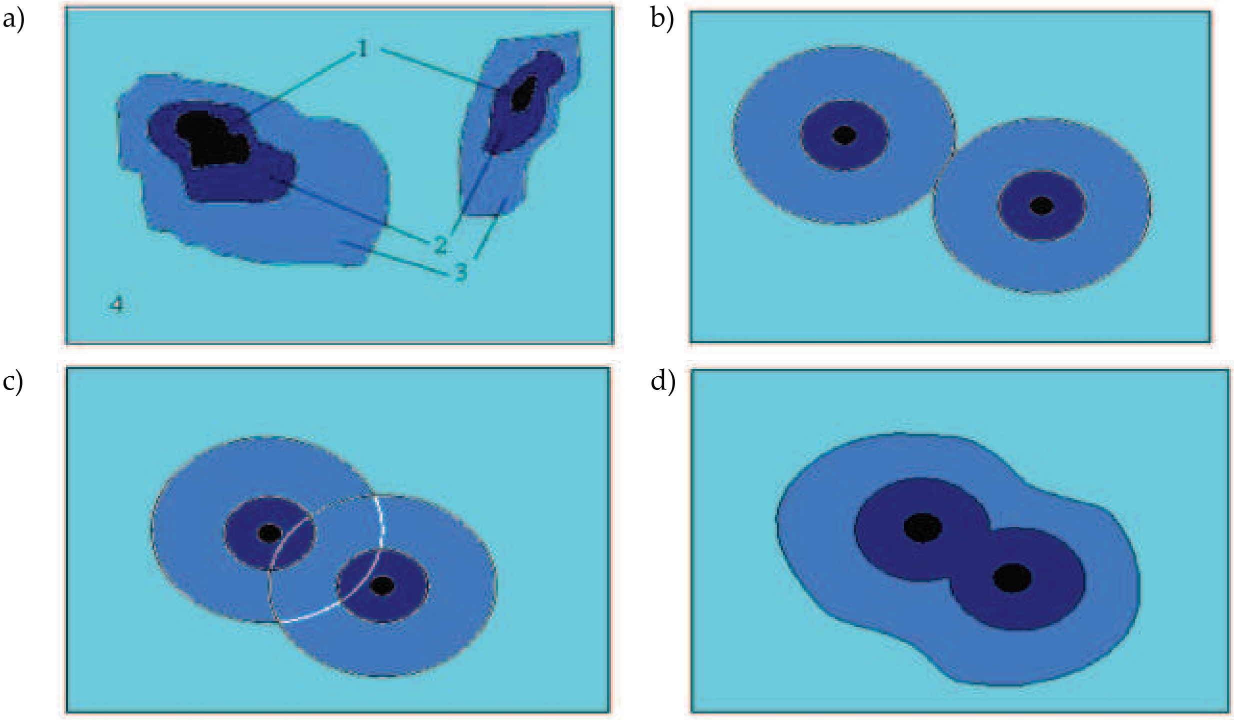

Fig. 1. Scheme of ESL process forming: 1 – dispersion filler grain; 2 - surface layer as ESL component defined by the grain surface properties; 3 – ESL round the grains in the matrix material; 4 – composite gel-fraction zones; a) macromolecules migration, ESL forming initiation; b) ESL forming; c) ESL interpenetration; d) cluster forming in the composite structure

Rys. 1. Schemat procesu powstawania zewnętrznej warstwy powierzchniowej (ZWP): 1 – rozproszone ziarna napełniacza, 2 – warstwa powierzchniowa jako składowa ZWP, zredefiniowana przez właściwości powierzchni ziarna, 3 – ZWP wokół ziarn w matrycy, 4 – kompozytowe strefy frakcji żelowe; a) migracja molekularna, zapoczątkowanie powstawania ZWP, b) tworzenie się ZWP, c) wzajemne przenikanie ZWP, d) tworzenie klastra w strukturze kompozytu matrix binding in ESL and its volume percentage in the polymer, which defines the operation characteristics of the composite materials (Fig 1, Fig 2 and Fig 3). Hard surface of the filler causes the change of conformation choice of macromolecules and supermolecules structure near its surface. These parameters were found according to the number of paramagnetic centers on the phase interface taking advantage of the electron paramagnetic resonance method.

The number of mentioned centers depends on the filler activity relatively the polymer matrix as well as on the binding viscosity (Fig. 2). Hardening result in formation of ESL different extent and density around the filler.

Influence of the filler nature characteristics on ESL forming was determined. Taking into account the fact, that the binder in the ESL area is of another density, thus the degree of binding different from those of the polymer matrix

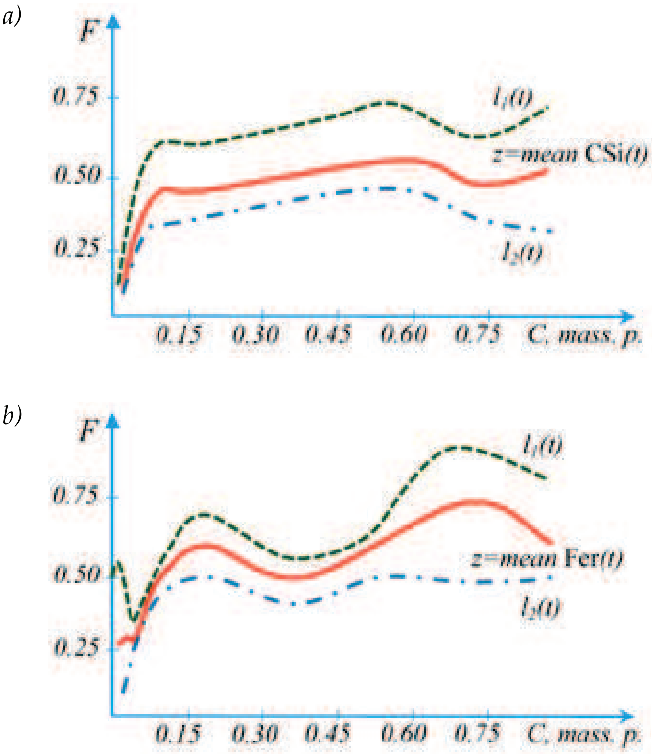

Fig. 2. Dependence of the active centers concentration in the particle surface on the content of the dispersion fillers: silicon carbide and ferrite correspondingly

Rys. 2. Zależność stężenia centrów aktywnych na powierzchni cząstek od zawartości napełniaczy: a) węglika krzemu, b) ferrytu

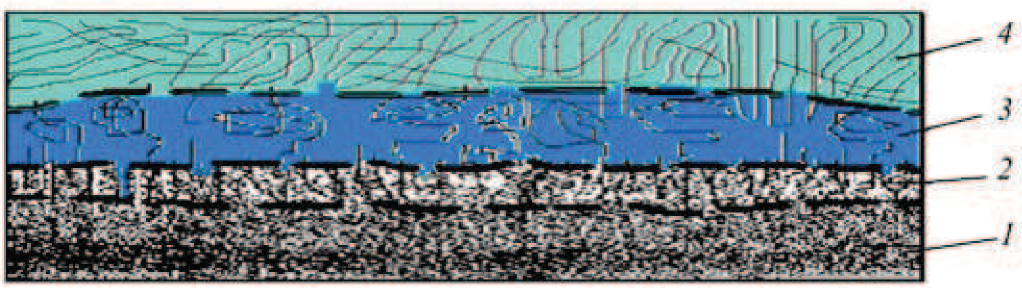

Fig. 3. Scheme of ESL structure in composites. Notation as in Figure 1

Rys. 3. Schemat struktury zewnętrznej warstwy powierzchniowej w kompozytach. Oznaczenia jak na rysunku 1 and the dispersion filler, it possesses different optical characteristics, such as illumination gradient change while transition from the filler to the matrix.

To improve the method of finding ESL the mathematics model of resource exchange while epoxide-composite hardening and the choosing the grain size function reading has been proposed.

The influence of topological-geometric characteristics of ESL around the dispersion particles of the filler in the composite matrix on the physical-mechanical characteristics of composite material has been proved [9]. The process of ESL forming is expected to be revealed in some stages:

– migration of the epoxide oligomer macromolecules to the phase interface "oligomer binder-filler",
– ESL formation around dispersion or fiber filler,
– formation of the penetration areas and microfracture of physical bonds between macromolecules,
– ESL clusterisation in the matrix volume.

During investigations thin composite film with separate particles were made, when the film thickness was in two times larger than that of the dispersion particle. In further investigations the processing of numerical images was performed. To prove the expectations method of the numerical analyses of this image characteristics have been proposed. Estimation of the CM structural parameters was carried out taking advantage of the optical devices and MathCAD-base software taking pictures in BMP formats in 5–15 min interval from 0 till 300 min of hardening.

Such procedure of investigation made possible to improve the visualization quality of the ESL kinetics. While identifying the ESL characteristics the matrix (data file) was obtained, each element of which corresponds the development intensity of every image pixel within 0–255 nominal units.

$$A = READBMP\,(F), \quad A = (a_{i,j}), \qquad 0 \le a_{i,j} \le 255$$

Having separated the fragment of mass A, which corresponds the investigated object, using the sequence application of discrete, two-dimensional Furrier's transformation K and anhedral to it KK, ignoring noises and illuminations trends on the fragment, the accuracy of ESL visualization could be improved.

$$P = submatrix(A, r_1, r_2, c_1, c_2), \qquad K = cfft(P)$$

$$g_{i,j} = if(k_1 \le |K_{i,j}| \le k_2, K_{i,j}, 0), \qquad KK = icfft(g)$$

Investigated gradient field makes possible to estimate the accuracy of the material structure characteristics in the chosen object fragment, that is, matrix structure in ESL around the filler part. Performed transformations make possible to outline the object illegibly, geometry of which depends on the degree of the image grain size (granularity), and, thus, on the materials structure [10, 11].

$$G_{i,j} = \sqrt{(nx_{i,j})^2 + (ny_{i,j})^2}, \qquad n_{i,j} = \frac{mean\,(D_{i,j})}{\mu}$$

$$nx_{i,j} = \frac{n_{i+1,j+1} - n_{i-1,j+1} + n_{i+1,j-1} - n_{i-1,j-1}}{4h_1}$$

$$ny_{i,j} = \frac{n_{i+1,j+1} - n_{i+1,j-1} + n_{i-1,j+1} - n_{i-1,j-1}}{4h_2}$$

Basing on the obtained matrixes, the diagrams, which make possible to estimate geometric parameters of ESL are built their area thickness in particular. Having known the particle topology and ESL volume in the composite material, the process of ESL forming in epoxide-composites since the time of hardening, can be investigated. Methods of comparison projection and cross-section areas of ESL in the particle threshold (Fig. 4) have been used.

The results of investigations of composite materials microstructure make possible to state, that ESL formed around the dispersion particles of the filler during the composite hardening grave unevenly in time and are not equally retarding, which must be taken into account while creating new materials. Further investigations delt with the building of models for the ESL propagation along the main lines. Kinetics of metric changes of such layers can be specified as the combination of asymptotically descending and damping oscillation processes. Limit speeds of propagation and the ESL length for every type of the filler have been found. It was determined, that the largest ESL size are obtained during the first 60–120 min of hardening. The most effective ESL extent after completing the process of hardening (72 hours) was 53.1 µm, the highest limit propagation speed – 12.7 µm/min was noticed for the ferrit filler.

Further the degree of ESL binding was investigated (Fig. 5). It was found, that in the threshold of the filler particle threshold the created material is of rather high density: 1300kg/m^3 for the brown slime and 1500 kg/m^3 for copper oxide. The matrix is of 1100–1120 kg/m^3.

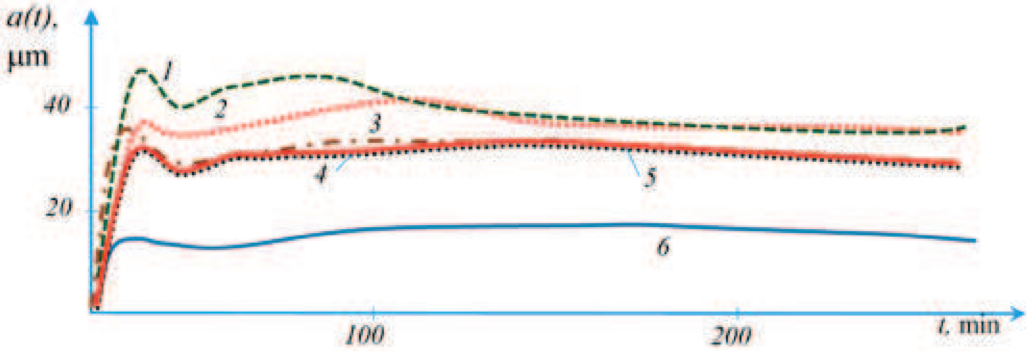

Fig. 4. ESL thickness obtained by cross-section method for the 63 µm dispersion particles. Fillers: 1 – ferrite, 2 – copper oxide, 3 – boron carbide, 4 – electro corundum, 5 – silicon carbide, 6 – brown slime

Fig. 4. Grubość ZWP otrzymana metodą badania przekroju poprzecznego przy rozmiarach cząstek napełniacza 63 µµ: 1 – ferrytu, 2 – tlenku miedzi, 3 – węglika boru, 4 – elektrokorundu, 5 – węglika krzemu, 6 – brązowego szlamu

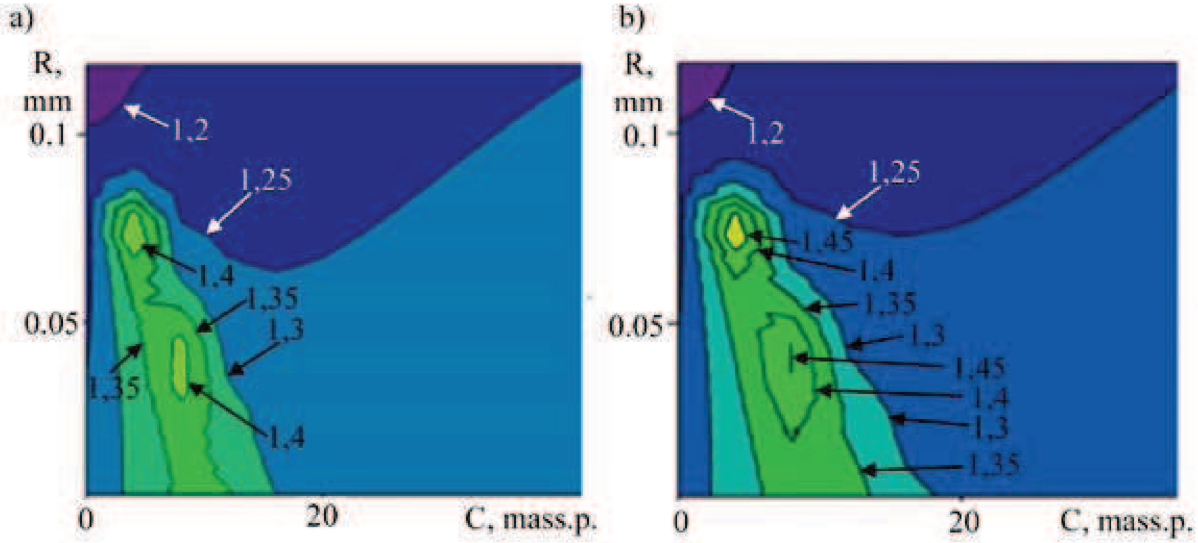

Fig. 5. Diagrams of the ESL density dependence on the composite content and the distance between the filler particles: a) silicon carbide; b) electro corundum

Rys. 5. Diagramy zależności gęstości ZWP od zawartości masowej napełniacza i odległości pomiędzy cząstkami dla: a) węglika krzemu, b) elektrokorundu

Maximum ESL parameters and its kinetics have been found. Then residual stresses and adhesion strength of the material were studied. Minimum residual stresses under high adhesion strength are obtained for the content of 20–25% of ESL. Material with content of 55% corresponds the optimal damping properties and high wear-resistance of the material. 85% of its content corresponds the highest cohesion strength for every of 40–60 μm dispersion fillers. For small dispersion ones, 10–30 μm, filler (TG, CB, BS) 30%, 60% and 90–95% ESL content correspondingly are obtained. That is why we propose to use multi-layer coatings, which specify physical-mechanical properties, which are affected by the ESL content percentage. That is why to improve the operation characteristics multylayer coatings are proposed to be applied, which contain different amount of the matrix material in ESL, which density affects the physical and mechanical properties of the material as a whole. It will make possible to propose new technological regimes of composite materials forming.

Then the investigations of composite physical-mechanical properties of composites have been carried out. It was found, that during initial process of the composite forming (40–60 min) the growth of the residual stresses in the material was noticed (1.1% for the electro corundum and 4% for copper oxide), and the decrease of fracture stresses under bending (by 0.6% and 1.6% correspondingly) for every 10% of increasing of the ESL volume. In other time intervals, the dependence monotony is ruined. Basing on the results of the analysis of different fillers content in the matrix, its maximum values in the composite materials were found. Critical points on the diagrams of the correlation dependences of the residual stresses and fracture stresses under bending were found in the conditions of the monotony change of both characteristics while increasing the filler content. Choosing the maximum filler content among variety of critical points, the methods of tasks for the object classification were used. Here the main condition was, that in composite materials with the improved physical-mechanical properties, residual stresses must be minimal, and the value of the fracture stress under bending must be maximal. It makes possible to determine the influence of the filler amount, under which the residual stresses decrease from 20% to 50%, and fracture stresses under bending increase by 18–45%.

Maximum content of the dispersion filler in the composite materials was found while investigating: threshold relation of the absolute values of the residual stresses to the adhesive strength of composites; comparison of the growth rates of the residual stresses and adhesive strength dependencies. Thus, let us find the range of the maximum content of the investigated fillers in composites as well as the range of the particles content for the materials, which can not be recommended for the long-term application as the protective coatings. Substantial increase of the operation characteristics of composite materials was obtained while providing optimal conditions of interaction on phase interface "filler-binder", sufficient degree of matrix binding in ESL and increase of the "rigid" ESL extent in the polymer matrix volume. It can be obtained while introducing of two fillers of different nature, size and content into the epoxide oligomer. It was found, that introduction of the polydispersion two-component filler into the binder at maximum content increases the impact viscosity by 11–33%, fracture stress under binding by 40–50%.

The next stage of investigations of composite materials was determination of the fiber filler influence on the ESL forming and the effect of the ESL volume on their physical-mechanical properties. Besides, important from the scientific point of view was the investigation of ESL in the system "binder-dispersion and fiber filler" undergoing the effect of energy fields. Dynamics of the modulus of instantaneous elasticity of composite materials taking into account the characteristics of composite materials at different stages of binding of epoxyplasts untreated and irradiated by the ultraviolet rays containing of binding of epoxyplasts untreated and irradiated by the ultraviolet rays containing dispersion and fiber. Basalt and glass fibers were used as reinforcing fillers. General analysis of the results of investigation makes possible to state: introduction of the dispersion filler, despite its physical nature, results mainly in the increase of the structure-forming processes rate. The curve (Fig. 6) of change dependence of shear modulus value on the duration of the composite hardening is characterized by the special shape with two plate areas and three inflection points, is of the step-by-step nature and not smooth in definite points (about 7.5 hours, 27.5–30 hours, 55–66 hours of binding time correspondingly).

That is why the further stage was the building of the ESL forming model around the filler: fibers and dispersion particles. According to the change of the angle tangent mechanical losses in time and taking advantage of the torsion pendulum the effect of different fillers and the way of modification on the binding processes of the polymer matrix in the composite materials have been found. The ESL volume was measured using the Takayanagy's model, which takes into account the change of the filler volume while hardening. The obtained results show testify the high level of correlation between the shear modulus and total thickness of ESL while forming composites. The highest values of correlation is obtained in the case of combined fillers, which have been irradiated by the ultraviolet rays before. It is confirmed by the effect of the ESL extent on the physical-mechanical characteristics of composites under the stable conditions of the material ingredients. Every per cent of the ESL extent growth (4–8 mm) causes the shear modulus increase from 0.8 MPa at the beginning till 2.3 MPa at the completion of forming [11, 12].

Analytical expressions of the modulus of instantaneous shear in time for composites with glass, basalt and carbon fibers look like:

$$hs(t) = 0{,}984 + 0{,}898 \cdot arctg(0{,}065t - 1{,}69);$$

$$hb(t) = 1{,}126 + 1{,}337 \cdot arctg(0{,}043t - 1{,}20);$$

$$hv(t) = 0{,}717 + 1{,}009 \cdot arctg(0{,}039t - 0{,}95).$$

Investigation of the ESL forming kinetics and the change of physical-mechanical properties of composite can be used to predict the operation characteristics of coatings taking advantage of introduction of multi-component dispersion and fiber fillers of different physical-chemical nature.

It was found, that in order to decrease the material creep, especially in the harmful environment, it is worth using two-layer epoxide composite materials, containing glass and basalt fibers. To increase the operation characteristics of composites as the intermediate layer it is recommended to use irradiated by the ultraviolet rays plasticized epoxide binder, containing dispersion filler parts preliminary modified by the epoxide oligomer. Basing on the investigations of the ESL change in time undergoing the action of different fillers as to their activity, both dispersion and fiber, new technologies of the materials forming have been proposed at the initial stages of ESL forming. For the additional improvement of composites characteristics UVI and USM were used, which will result in the creation of materials with the improved operation characteristics [13].

4. CONCLUSION

Objects of industrial application have been chosen basing on the laboratory and industrial investigations of the developed materials in the conditions of sign-variable loadings and sufficient temperature-variable gradient. Complex experimental investigations and applications of the developed coatings have testified them being expedient and possessing high effectiveness for application in different branches of in-

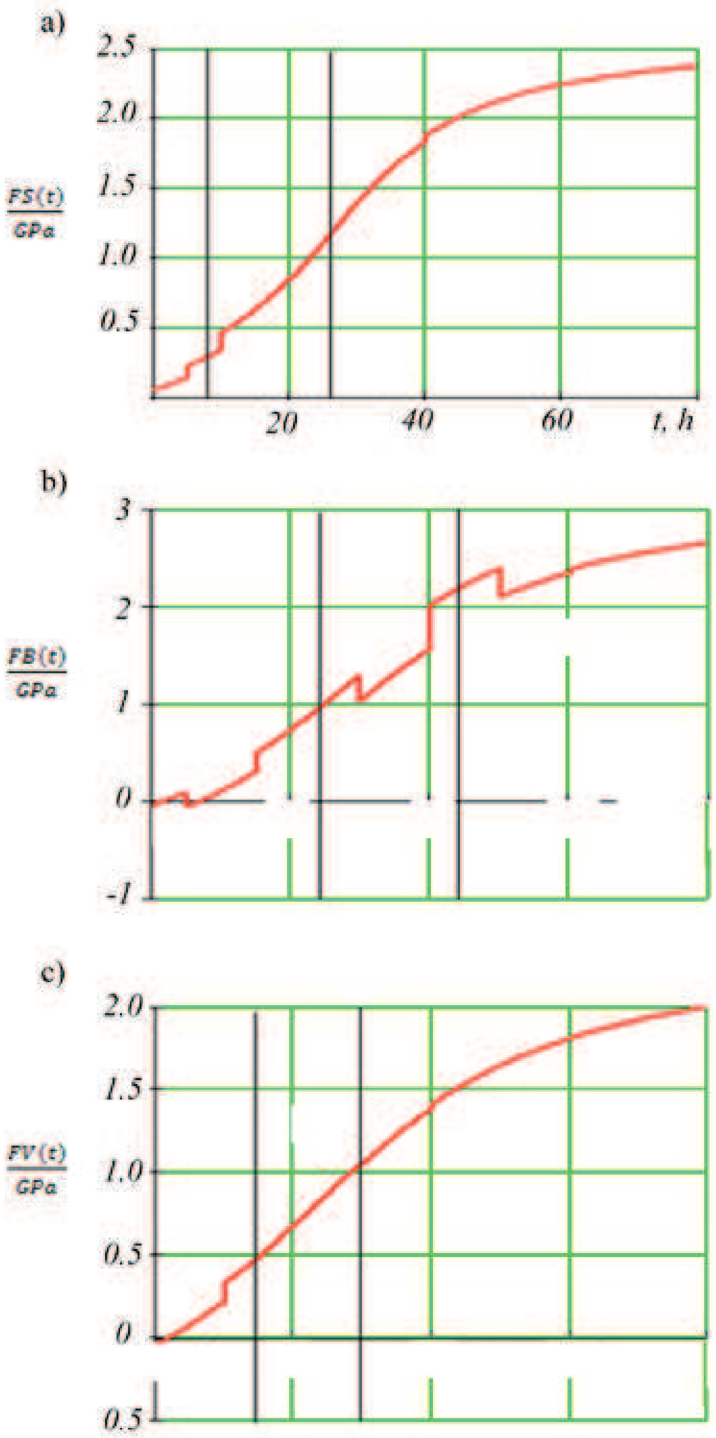

Fig. 6. Dependence of shear modulus on the time of hardening of composite material with fillers: a) glass fibers, b) basalt fibers, c) carbon fibers

Rys. 6. Zależność współczynnika sprężystości poprzecznej od czasu utwardzania materiału kompozytowego z napełniaczem w postaci: a) włókien szklanych, b) włókien bazaltowych, c) włókien węglowych dustry. Their introduction at the tested objects has testified, that application of protective coatings is very efficient to withstand corrosion of metal constructions and equipment in harmful environments, as well as atmosphere effect, providing raising of the corrosion durability in 2.5–2.7 times. Besides, application of the developed composite materials provides increase of wear reliability and durability of the equipment in 2–3 times, which results in the increase of the scheduled maintenance period in 3.0–3.5 times.

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