ADHESIVE INTERACTION IN HYBRID POLYMER COMPOSITES. ENERGY CHARACTERISTICS OF PHASES AT THE AIR INTERFACE

Almaz Valiev1*, Irina Starovoitova², Alfred Suleymanov¹

¹ Kazan University of Architecture and Civil Engineering, Kazan, Russia

2 LLC "Research and Production Company "Rekon", Kazan, Russia

*Corresponding author's e-mail: tatcomposite@mail.ru

Abstract

Introduction: The study of the adhesive strength formation mechanisms in polymer composites involves the deliberate selection of components to facilitate their joint action in transferring stresses from the fibers to the binder through the phase interface. The strength of the adhesive interaction between components can be expressed through their energy characteristics, provided technological and other factors are ensured. **Purpose of the study:** The study aims to investigate the energy characteristics of hybrid polymer composite phases at the air interface. **Methods**: The optical method was used to capture micrographs of wetting fibers of different nature by liquids, based on which contact angles were determined. Tensile tests of fibers were conducted, and thermal analysis of fibers was performed using a synchronous thermal analyzer. The surface tension of epoxy resin and the epoxy resin / hardener system was determined using a tensiometer. **Results**: The method for determining surface energies of solids was upgraded. The upgraded method makes it possible to determine the free surface energy of fibers of different nature and the surface tension of the binder. The effect of oiling compositions (finishing agents) was quantitatively evaluated.

Keywords: composite, hybrid, adhesion, wetting, adhesion action, free surface energy.

Introduction

Polymer composite is a system with a complex hierarchical structure, the components of which differ significantly in their elastic-mechanical and thermophysical characteristics (Kayumov and Shakirzyanov, 2021; Mercier et al., 2021; Zheng and Guo, 2021).

Hybrid composites are composites that contain more than one type of reinforcing component in the matrix. An additional reinforcing component is included to improve the elastic-mechanical characteristics of the material (in particular, to reduce strains) and makes it possible to obtain structures with optimal balanced properties (Gunyaev, 1977; Skudra and Bulavs, 1978). In construction, these materials are used in pedestrian bridge structures, etc. As a rule, such products are manufactured using the vacuum infusion technology in accordance with GOST 27751–2014.

The fiber/matrix interfacial region contributes significantly to the elastic-mechanical properties of the finished composite. At maximum effect, it allows for using the filler strength to a large extent (Hughes, 1991; Kim and Mai, 1998). During binder curing, due to chemical reactions between the resin and the hardener as well as spatial reorientation of molecules, parameters of the free surface energy of the binder change with time and reach maximum values only after complete curing.

The interaction between two condensed phases results in a physical or chemical bond, which can

be evaluated by its strength. As known, there are several adhesion theories: mechanical, electrical (electronic), adsorption (molecular), relaxation, and weak layer theories. Each of the theories was developed to explain the basic mechanisms of adhesion contact formation. Regulation of interfacial interaction properties makes it possible to reduce residual stresses in the finished product and obtain the required physical and mechanical properties.

In case of fiber composites, the fracture strength is determined by the adhesive strength of the fiber/ binder bond (τ_0) , and wetting is the most important process in the occurrence of bonding between the reinforcing filler and binder at the phase interface (Kramarev et al., 2017; Shakhmurzova et al., 2022). The adhesive strength of the fiber/ binder bond can be determined by both micro- and macromechanical tests (pull-out method, pushout method, fragmentation method, methods of finished composite product failure under shear, bending, etc.) (Gulyaev et al., 2019; Zhang, 2012). Despite the variety of methods, adhesive interaction is considered a statistical value, which is mainly determined by the random distribution of defects at the phase interface, hence it can be observed that the results of adhesive strength determination are sensitive to the specimen size.

Adhesive interaction at the phase interface in the matrix-filler bond depends on a wide range of factors. The strength of adhesive interaction between components can be expressed through the energy

characteristics of the surface: thermodynamic work of adhesion (W_a) , free surface energy and its dispersion and acid/base components (γ^d, γ^{ab}) (Karzov et al., 2010). Various wetting methods (sessile drop method (Danilov et al., 2019), sitting drop method, method of determining the contact angle of an elementary fiber using a cuvette with liquid, mounted on a horizontal microscope, Washburn method, Adam-Schütte method, etc.) using test liquids with known free surface energy parameters (Starostina and Stoyanov, 2010) are prioritized in this respect since the experimental determination of free surface energy parameters is quite effort-consuming in practice.

The surface tension of liquids is also measured by various methods (Wilhelmy plate method (Wilhelmy, 1863), Du Nouy rings (Lecomte du Nouy, 1925), etc.). These measurements determine surface tension by measuring the force acting on the object immersed in a liquid (plates, rings, etc.) and the length of the wetted surface.

Estimating the parameters of the free surface energy of phases in a hybrid composite with a combination of fibers of different nature is a key task in predicting elastic-mechanical properties and optimizing the selection of components.

The energy of wetting solid surfaces to determine the chemical nature when determining the contact angle is also related to numerous factors (wetting hysteresis, surface roughness, test temperature and humidity).

The thermodynamic work of adhesion and parameters of free surface energy between liquid and solid phases can be determined by experimental measurements of the contact angle of wetting of a solid surface by liquids with known free surface energy parameters using various equations (Young– Dupre (Dupre, 1869), Owens–Wendt (Owens and Wendt, 1969), Vann Oss–Chaudhury–Good (Vann Oss et al., 1989), etc.). Among them the Vann Oss– Chaudhury–Good theory has the priority. According to this theory, three test fluids with known free surface energy parameters should be used to determine the free surface energy of a solid surface by solving a system of equations with three unknowns.

According to the Vann Oss–Chaudhury–Good theory, the thermodynamic work of adhesion and free surface energy parameters are determined by equation (1) (Vann Oss et al., 1989):

$$
W_a = \gamma_I \left(1 + \cos \theta\right) =
$$

= $2 \left(\gamma_I^d \gamma_s^d\right)^{1/2} + 2 \left(\gamma_I^+ \gamma_s^-\right)^{1/2} + 2 \left(\gamma_s^+ \gamma_I^-\right)^{1/2},$ (1)

where:

- γ^+ acid parameter;
- $\gamma^{'}$ base parameter;
- γ*d* dispersion parameter;
- l liquid phase;
- *s* solid phase;

For a bipolar substance, the acid/base component (γ^{ab}) is determined by equation (2):

$$
\gamma^{ab} = 2\sqrt{\gamma^+}\sqrt{\gamma^-}.
$$
 (2)

It should be noted that test fluids also include monopolar fluids. For example, neutral hydrocarbons (n-hexane) have zero acid/base components of free surface energy, while the full value is 18.43 mJ/m² $(\gamma_l = \gamma_l^d)$. This type of test fluid is used in selective wetting.

The parameters of the free surface energy of solid surfaces are usually determined by linear approximation, where the resulting solution of the system depends on the choice of test fluids and is unstable (Starostina and Stoyanov, 2010).

The problem of obtaining a general solution for the parameters of the free surface energy of solid surfaces was solved by Starostina et al. (2013) by transforming equation (1) to the equation of plane $z = Ax + By + C$:

$$
\frac{\gamma_I (1+cos\theta)}{2\sqrt{\gamma_I^-}} = \frac{\sqrt{\gamma_I^d}}{\sqrt{\gamma_I^-}} \sqrt{\gamma_s^d} + \frac{\sqrt{\gamma_I^+}}{\sqrt{\gamma_I^-}} \sqrt{\gamma_s^-} + \sqrt{\gamma_s^+}. \quad (3)
$$

A more accurate way to find the unique values of the parameters of the free surface of solid surfaces is by the spatial three-dimensional method rather than by linear approximation, as was previously done by researchers (Starostina et al., 2011; McCafferty, 2002). Based on the spatial method, the free surface energy parameters of a large number of solid surfaces (polymers, polymer composites, glass, metals) were estimated. The spatial threedimensional method has not been used to determine the free surface energy parameters of elementary fibers of different nature.

This study aims to investigate the energy characteristics of hybrid polymer composite phases at the air interface. The objectives of the study are as follows: (1) determining the variation in the free surface energy parameters of elementary fibers of different nature to investigate the contribution of oiling compositions and finishing agents, using the spatial method and the Vann Oss–Chaudhury– Good theory, (2) determining the surface tension of low-viscosity epoxy resin and binder (Du Nouy rings method), (3) estimating the contact angle of elementary fibers with binder for vacuum infusion.

Subject, tasks, and methods

To determine the variation in the free surface energy parameters of hybrid polymer composite components, estimated by the contact angle, and analyze their wetting, the following materials were used:

1. Fiber reinforcing fillers:

a) Unidirectional carbon fabric FibArm Tape 230 manufactured by JSC Umatex, Rosatom State Corporation (Technical Specifications 1916-018- 61664530–2013).

b) Unidirectional glass fabric (tape) Ortex 400 O 250 manufactured by BauTex (Technical Specifications 13.20.46.000-006-52788109–2019).

c) Basalt woven fabric BNPP-B-10-610-KV-41 (Technical Specifications 5952-007-13307094-12) manufactured by LLC Kamenny Vek.

2. Modified epoxy resin L for vacuum infusion.

3. Hardener GL2 manufactured by R&G Faserverbundwerkstoffe GmbH, Germany (ratio resin L / hardener GL2 — 100:30, viscosity at 25 °C — 248 ± 100 mPa·s).

Fiber calcination with the aim to remove the initial oiling composition (finishing agent) was carried out in a muffle furnace preheated to a temperature of +420 °C for carbon fiber and +560 °C for glass fiber based on the evaluation of thermal characteristics of fabrics with the use of an STA 6000 synchronous thermal analyzer. Heating rate: 10±1 °C/min.

The fibers with initial oiling compositions (finishing agents) and after annealing were tensile tested using cardboard overlays and cyanoacrylate adhesive to prevent the specimens from slipping out. In case of glass fiber, the linear density according to the technical data is 1200 tex, in case of carbon fiber $-$ 800 tex, the length of the working area $-$ 100 mm. The calculations used only data on testing the specimens in which failure occurred between the clamps in the working area.

With the use of the optical method with horizontal positioning of an MPSU-1 simplified stereoscopic microscope (with 4.8^x optical head magnification) and attachment of an AmScope SLR/DSLR adapter (with 2 magnification) compatible with Nikon D3100 camera (14.2 megapixels) (total magnification — 9.6), micrographs of wetting glass, carbon and basalt elementary fibers were obtained for different test fluids with known free surface energy parameters:

a) distilled water according to GOST R 58144– 2018;

b) aniline according to GOST 5819–78;

c) ethylene glycol according to GOST 10164–75.

Table 1 shows the free surface energy parameters of the test fluids, mJ/m², at T = 20 °C.

The contact angle was determined based on video and micrographs of the meniscus during the elementary fiber movement, with the use of the AutoCad graphic environment, by drawing a

Table 1. **Surface energy and its components for test fluids**

| Test fluid | γ_I | v_i^q | γ_i^+ | γ_{1} | v_1^{ab} |
|-------------------|------------|---------|--------------|--------------|------------|
| Distilled water | 72 | 22 | 28.34 | 22.23 | 50 |
| Aniline | 43.2 | 41.2 | 0.18 | 5.71 | |
| Ethylene glycol | 48.3 | 29.3 | 12.08 | 7.47 | 19 |

tangent line. The air temperature during the test was $+(20±2)$ °C, air humidity was ~55 %. Fig. 1 shows a scheme for determining the contact angle.

The free surface energy parameters of the epoxy binder for vacuum infusion directly depend on the epoxy and hydroxyl groups (in general, their amount is determined according to GOST 17555–72) of the resin and on the type and characteristics of the hardener. According to the technical data, resin L is an epoxy resin based on bisphenol (A+F), diluted with a bifunctional compound, and is characterized by low viscosity (at 25 °C $-$ 710 \pm 70 mPa·s), lack of solvents, fillers, nonylphenol and benzil alcohol in the composition; the epoxy value is 0.56 (100/eq), and the epoxy equivalent is 179 (g/eq). Due to the high reactivity of epoxy groups and the presence of hydroxyl groups, different methods of epoxy resin curing can be selected. Hardener GL2 is a composition based on a mixture of aliphatic and cycloaliphatic amines. The curing of resin L with hardener GL2 is almost shrinkage-free.

The surface tension of low-viscosity epoxy resin L and the resin L + hardener GL2 system (component ratio 100:30) was determined based on the Du Nouy rings method on a TD 3 Lauda tensiometer.

Results and discussion

Inorganic (glass and basalt) and carbon fibers undergo oiling or finishing stages (with oiling compositions or finishing agents where aqueous dispersions of organic resins are the film-forming component). This process step ensures the manufacturability of fiber processing, in particular, protecting fibers against mechanical damage as well as improving adhesion between the fibers (reinforcing filler) and the binder (matrix) when obtaining polymer composite materials. To investigate the contribution of oiling compositions and finishing agents, it is necessary to study the issue of their removal as well.

In research literature, the following is distinguished regarding the removal of the oiling compositions (finishing agents) of fibers: washing with organic solvents or pyrolysis in a muffle furnace at high temperatures. It should be noted that even with repeated washing of fibers in organic solvent solutions, a part of the oiling composition (finishing agent) remains in the preforms, while pyrolysis ensures almost complete removal (this method is more environmentally friendly compared to washing with organic solvent solutions) (Petrova and Beider, 2016).

A thermal decomposition method was selected for the removal of the oiling composition (finishing agent). Temperature ranges of thermal decomposition of the initial oiling compositions (finishing agent) of fabrics were determined by thermogravimetric analysis. Figs. 2–4 show the results in the form of TG-DTG, DTA thermal analytical curves for glass, carbon, and basalt fabrics, respectively, weight variation in the range of 30–850 °C (% wt.) is presented in Table 2.

Fig. 1. Scheme for determining the contact angle (θ): (1 — elementary fiber, 2 — test fluid, 3 — weight, 4 — cuvette, 5 — mechanical platform, 6 — holder of elementary fiber, 7 — horizontal microscope, 8 — moving mirror (with a light source))

Based on the results of thermogravimetric analysis (TG curve), it can be inferred that the weight loss in case of glass fabric occurs at 200– 560°C (–0.64 % wt.) in case of carbon fabric — at 130–420°C (–1.47 % wt.), in case of basalt fabric at 170–600°C (–1.11 % wt.), and it is obvious that this is largely due to the removal of the oiling composition (finishing agent). It can be assumed that further weight loss is due to thermal degradation of the material. GOST 6943.1–2015 regulates the conditions of oiling composition (finishing agent) removal from the surfaces of glass and carbon fibers, and it is recommended to perform calcination of

fibers in a muffle furnace preheated to a temperature of (625±20)°C during 20–30 minutes for glass fibers, and to a temperature of (450±5)°C during 15–25 minutes for carbon fibers. The TG results and the GOST 6943.1–2015 recommendations are close in values, therefore, all subsequent studies were conducted on materials pre-annealed at 560°C for 30 minutes in case of glass fabric, at 420°C for 25 minutes in case of carbon fabric, and at 600°C for 30 minutes in case of basalt fabric.

Fig. 5 shows the histograms of residual tensile strength for glass and carbon fibers after annealing at different temperatures.

Fig. 2. TG-DTG, DTA thermal analytical curves for glass fabric (red — TG curve, green — DTG curve, blue — DTA curve)

265.43 °C
-0.065 %/mi

| No. | Fabric type | | Weight change in the range of 30-850°C, % wt. | | | | |
|---------------|-------------------------|---------------------------|--|----------------------------|----------------------------|----------------------------|---------|
| | Glass fabric I | $30 - 200 (-)$ $+0.21$ | 200-410 (294) -0.56 | $410 - 560$ (-) -0.08 | $560 - 850 (-)$ $+0.05$ | | -0.38 |
| \mathcal{P} | Carbon fabric | $30 - 130 (-)$ $+0.21$ | $130 - 300 (-)$ -0.57 | 300-420 (365) -0.90 | 420-580 (507) -0.77 | $580 - 850$ (-) -4.79 | -6.82 |
| 3 | Basalt fabric | $30 - 170$ (- $+0.47$ | 170-440 (265) -1.09 | $440 - 600 (-)$ -0.02 | $600 - 850$ (-) $+0.23$ | | -0.37 |

Table 2. **Temperature ranges of anomalies and fiber weight changes**

The relative breaking load for carbon fiber after annealing at 300°C increased slightly by 0.9 %, at 400°C — by 2 %, and at 420°C it decreased by 13.4 % (pyrolysis can also lead to the activation of its surface (increase in the specific surface area, sorption capacity (Khaskov et al., 2019; Nacharkina et al. 2021)); for glass fiber at 350°C, it decreased by 12.1 %, at 400°C — by 34.4 %,

 θ ä

 \mathcal{A} \overline{a} à. -1.0

> at 560°C — by 98.5 %; the similar was true for basalt fabric as well.

> Patterns of wetting glass, carbon, and basalt elementary fibers with test fluids were obtained by the optical method and then analyzed. Table 3 shows the results of determining the contact angles of fibers of different nature with test fluids, resin L, and binder. Measurement error — up to 10–15 %

Fig. 5. Histograms of residual tensile strength for glass and carbon fibers after annealing at different temperatures

(e.g., for angles $\sim 10^{\circ}$, the error is $\pm 1^{\circ}$, for angles \sim 18–30°, the error is \pm (2÷3)°).

In Eq. 3, all the characteristics of the test fluids, as well as the contact angles presented in Table 3, are known. Three values are unknown: the dispersion component as well as the acid and base parameters of the same characteristic. With the use of multivariate approximation, planes in coordinates y, z) were built, which are known values $\frac{\sqrt{\gamma}}{\sqrt{\gamma}}$ γ y γ $\gamma_I(1+\cos\theta)$ γ *l d l l l l* $\frac{1}{l}$ $\sqrt{\gamma_l}$ $2\sqrt{\gamma_l}$ $^{+}$ \overline{a} $\overline{$ $\frac{\sqrt{\gamma_l^+}}{\sqrt{n}}$; $\frac{\gamma_l(1+\cos\theta)}{\sqrt{n}}$). 2 Unknown are the values of the coefficients: A = $\sqrt{\gamma_s^d}$; B = $\sqrt{\gamma_s^-}$; C = $\sqrt{\gamma_s^+}$.

The coefficients were calculated automatically in the STATISTICA software. Three-dimensional planes demonstrating the obtained solution were also built there. For better accuracy, it is recommended to use as much data as possible on wetting fibers by fluids with known free surface energy parameters.

Fig. 6 shows the diagrams and equations of the approximated planes for glass and carbon elementary fibers; the same principle is used for basalt elementary fiber calculations.

Table 4 presents the free surface energy parameters of glass, carbon, and basalt elementary fibers with and without oiling compositions (finishing agents).

It should be noted that in the initial state (with oiling or finishing agent), carbon fibers have the lowest surface energy (18.72 mJ/m^2) and the contribution of the polar component is $~177$ %, glass and basalt fibers are characterized by high surface energy (38.31 and 33.98 mJ/m², respectively), and the contribution of the polar component is $~85$ %.

Based on the results of determining changes in the parameters of the free surface energy of fibers after removal of the oiling composition / finishing agent by pyrolysis, a decrease in their free surface energy is observed: by 15.3 % for glass fibers, by 22.3 % for carbon fibers; a decrease in the dispersion component (y_s^d) by 7.7 % for glass fibers and by 49.2 % for carbon fibers; a decrease in the polar component (γ_s^{ab}) by 16.6 % for glass fibers and by 14.3 % for carbon fibers; an increase in electronaccepting (acid) interactions (γ_s^+) by 12.9 % for glass and carbon fibers (wetting by polar fluids (water, etc.) improves, wetting by nonpolar fluids (aniline, etc.) deteriorates); a decrease in electron-donating (base) interactions (γ_s^-) by 39.6 % for glass fibers and by 37.1 % for carbon fibers.

Table 5 presents the results of determining the surface tension of low-viscosity epoxy resin L and

Fig. 6. Diagrams and equations of the approximated planes for: a) glass monofiber; b) carbon monofiber

Table 4. **Free surface energy and its components for different fibers**

Table 5. **Surface tension and viscosity of epoxy resin and resin/hardener system**

the resin L + hardener GL2 system (component ratio 100:30)» after 5 minutes of stirring (with the platinum ring already catalyzing the polymerization process) using the Du Nouy rings method.

Due to the introduction of hardener, having lower viscosity and representing a mixture of aliphatic and cycloaliphatic amines, into the modified epoxy resin, structural plasticization is observed, which is manifested in a sharp decrease in viscosity (more than 2 times), surface tension of the system — by 15.6 % after five minutes of stirring (due to the spatial reorientation of molecules). Therefore, it is reasonable to study wetting of elementary fibers of different nature both with epoxy resin and with the epoxy resin / hardener system.

Based on the results of determining wetting (Table 6) of elementary fibers of different nature in defect-free areas (without various inclusions) by lowviscosity resin L, it can be concluded that optimal

Table 6. **Contact angles of epoxy compositions**

wetting occurs in case of glass fiber, then — basalt fiber, and the worst — in case of carbon fiber, which is due to higher surface tension of low-viscosity resin L and a smaller difference in the polarities of the contacting phases. Measurement error — up to 10–15 % (e.g., for angles \sim 10°, the error is \pm 1°, for angles $\sim 16-20^\circ$, the error is $\pm (2 \div 3)^\circ$).

When a mixture of epoxy resin and hardener $(L + GL2)$ is used for wetting, the wettability of all types of fibers significantly increases, which is manifested in a multiple reduction of the contact angle — up to 3–5°, and can be attributed to a decrease in viscosity and surface tension in the system $(L + GL2$ compared to epoxy resin L).

Application of oiling compositions on the surface of glass and basalt fibers as well as finishing agents on the surface of carbon fibers ensures bonding of individual filaments providing comprehensive protection against mechanical damage, and positively affects fiber wetting (up to 3°) by increasing the polarity of the fiber surface by creating active areas that promote the formation of hydrogen bonds with the implementation of the van der Waals interaction between the surface of fibers of different nature and binder molecules, improving the interfacial adhesion.

Conclusions

This paper presents the results of evaluating the energy characteristics of phases at the air interface, affecting the adhesion interaction in hybrid polymer composites:

1. The method for determining surface energies of solids was upgraded. The upgraded method makes it possible to determine the free surface energy of fibers of different nature and the surface tension of the binder.

2. Pyrolysis in air slightly deteriorates the elasticmechanical properties of carbon fibers (by 13.4 % at 420°C), decreases free surface energy (by 22.3 %), significantly decreases the dispersion component (by 49.2 %), decreases the polar component (by 14.3 %); an increase in acid interactions was 12.9 %, a decrease in base interactions was 37.1 %. Pyrolysis in air of glass fabrics results in substantial losses of glass fiber strength (by 98.5 % at 560°C), decreases free surface energy (by 15.3 %), the dispersion component (by 7.7 %), and the polar component (by 16.6 %); an increase in acid interactions was 12.9 %, a decrease in base interactions was 39.6 %.

3. Quantitative evaluation (by changes in elasticmechanical properties, free surface energy and its components) of the effect of oiling compositions (finishing agents) was performed. It is reasonable to select these compositions with account for the free surface energy parameters of fibers of different nature to increase the interfacial adhesion in polymer composites.

References

Danilov, V. E., Korolev, E. V., Ayzenshtadt, A. M., and Strokova, V. V. (2019). Features of the calculation of free energy of the surface based on the model for interfacial interaction of Owens–Wendt–Rabel–Kaelble. *Stroitel'nye Materialy [Construction Materials]*, No. 11, pp. 66–72. DOI: 10.31659/0585-430X-2019-776-11-66-72.

Dupre, M. A. (1869). *Théorie mécanique de la chaleur*. Paris: Gauthier-Villars, 484 p.

Gulyaev, A. I., Medvedev, P. N., Sbitneva, S. V., and Petrov, A.A. (2019). Experimental research of "fiber-matrix" adhesion strength in carbon fiber epoxy/polysulphone composite. *Aviation Materials and Technologies*, No. 4 (57), pp. 80–86. DOI: 10.18577/2071- 9140-2019-0-4-80-86.

Gunyaev, G. M. (1977). Polycomponent high-modulus composites. *Polymer Mechanics*, Issue 5, pp. 685–692. DOI: 10.1007/ BF00860318.

Hughes, J. D. H. (1991). The carbon fibre/epoxy interface—a review. *Composites Science and Technology*, Vol. 41, Issue 1, pp. 13–45. DOI: 10.1016/0266-3538(91)90050-Y.

Karzov, I. M., Alent'ev, A. Yu. Bogdanova, Yu. G., Kostina, Yu. V., and Shapagin, A. V. (2010). Influence of energy characteristics of the fiber-binder interface on polymer composite strength. *Moscow University Chemistry Bulletin*, Vol. 65, Issue 6, pp. 384–391. DOI: 10.3103/S0027131410060106.

Kayumov, R. A. and Shakirzyanov, F. R. (2021). Large deflections and stability of low-angle arches and panels during creep flow. In: Altenbach, H., Eremeyev, V. A., and Igumnov, L. A. (eds.). *Multiscale Solid Mechanics. Advanced Structured Materials*, Vol. 141. Cham: Springer, pp. 237–248. DOI: 10.1007/978-3-030-54928-2_18.

Khaskov, M. A., Zelenina, I. V., Sorokin, O. Yu., and Gulyaev, A. I. (2019). Ceramic interfacial coating on carbon fibers based on polycarbosilane and oligovinylsilazane. *Glass Physics and Chemistry*, Vol. 44, Issue 6, pp. 601–606. DOI: 10.1134/ S108765961806010X.

Kim, J.-K. and Mai, Y.-W. (1998). *Engineered interfaces in fiber reinforced composites*. Oxford: Elsevier, 416 р.

Kramarev, D. V., Osipchik, V. S., Chalaya, N. M., Berezina, A. B., and Kolesnikov, A. V. (2017). Study of interfacial phenomena at the fiber–binder interface in imido-organoplastics. *Plasticheskie Massy*, No. 7–8, pp. 3–6. DOI: 10.35164/0554-2901-2017-7-8.

Lecomte du Nouy, P. (1925). An interfacial tensiometer for universal use. *Journal of General Physiology*, Vol. 7, Issue 5, pp. 625– 633. DOI: 10.1085/jgp.7.5.625.

McCafferty, E. (2002). Acid-base effects in polymer adhesion at metal surfaces. *Journal of Adhesion Science and Technology*, Vol. 16, Issue 3, pp. 239–255. DOI: 10.1163/156856102317295478.

Mercier, C., Khelil, A., Al Mahmoud, F., Blin-Lacroix, J.-L., and Pamies, A. (2021). Experimental investigations of buckling behaviour of steel scaffolds. *Structures*, Vol. 33, pp. 433–450. DOI: 10.1016/J.ISTRUC.2021.04.045.

Nacharkina, A. V., Zelenina, I. V., Valueva, M. I., and Voronina, O. G. (2021). Influence of additional sizing of carbon fiber in producing volume-reinforced preforms on the properties of high-temperature carbon fiber. *Scientific and Technical Journal "Proceedings of VIAM"*, No. 1 (95), pp. 54–65. DOI: 10.18577/2307-6046-2021-0-1-54-65.

Owens, D. K. and Wendt, R. C. (1969). Estimation of the surface free energy of polymers. *Journal of Applied Polymer Science*, Vol. 13, Issue 8, pp. 1741–1747. DOI: 10.1002/app.1969.070130815.

Petrova, G. N. and Beider, E. Ya. (2016). Development and research of finishing compositions for thermoplastic carbon plastics. *Scientific and Technical Journal "Proceedings of VIAM"*, No. 12 (48), pp. 65–73. DOI: 10.18577/2307-6046-2016-0-12-9-9.

Shakhmurzova, K. T., Kurdanova, Zh. I., Kalmykova, G. Z., Slonov, A. L., Beev, A. A., and Khashirova, S. Yu. (2022). Surface modification of fiberglass with high temperature sizing agents. *Proceedings of the Kabardino-Balkarian State University*, Vol. XII, No. 2, pp. 67–74.

Skudra, A. M. and Bulavs, F. Ya. (1978). *Structural theory of reinforced plastics*. Riga: Zinatne, 192 p.

Starostina, I. A. and Stoyanov, O. V. (2010). Development of methods for the evaluation of the surface acid-base properties of polymeric materials. *Bulletin of Kazan Technological University*, No. 4, pp. 58–68.

Starostina, I. A., Stoyanov, O. V., Makhrova, N. V., and Deberdeev, R. Ya. (2011). Application of test polymer surfaces for the determination of free surface energy parameters. *Doklady Akademii Nauk*, Vol. 440, No. 1, pp. 64–66.

Starostina, I. A., Stoyanov, O. V., and Sokorova, N. V. (2013). Determination of free surface-energy parameters using a spatial method. *Polymer Science Series D*, Vol. 6, pp. 157–159. DOI: 10.1134/S1995421213020135.

Vann Oss, C. J., Chaudhury, M. K., and Good, R. J. (1989). The mechanism of phase separation of polymers in organic media apolar and polar systems. *Separation Science and Technology*, Vol. 24, Issue 1–2, pp. 15–30. DOI: 10.1080/01496398908049748.

Wilhelmy, L. (1863). Ueber die Abhängigkeit der Capillaritäts-Constanten des Alkohols von Substanz und Gestalt des benetzten festen Körpers. *Annalen der Physik und Chemie*, Vol. 195, Issue 6, pp. 177–217. DOI: 10.1002/andp.18631950602.

Zhang, J. (2012). *Different surface treatments of carbon fibers and their influence on the interfacial properties of carbon fiber/ epoxy composites*. [online] Available at: https://tel.archives-ouvertes.fr/tel-01146459 [Date accessed: September 10, 2023].

Zheng, Y. and Guo, Z. (2021). Investigation of joint behavior of disk-lock and cuplok steel tubular scaffold. *Journal of Constructional Steel Research*, Vol. 177, 106415. DOI: 10.1016/J.JCSR.2020.106415.

АДГЕЗИОННОЕ ВЗАИМОДЕЙСТВИЕ В ГИБРИДНОМ ПОЛИМЕРНОМ КОМПОЗИТЕ. ЭНЕРГЕТИЧЕСКИЕ ХАРАКТЕРИСТИКИ ФАЗ НА ГРАНИЦЕ С ВОЗДУХОМ

Валиев Алмаз Илсурович*¹, Старовойтова Ирина Анатольевна², Сулейманов Альфред Мидхатович¹

1 Казанский архитектурно-строительный университет, г. Казань, Россия 2 ООО «Научно-производственная фирма «Рекон», г. Казань, Россия

*E-mail: tatcomposite@mail.ru

Аннотация

Введение. Исследование механизмов формирования адгезионной прочности полимерных композитов заключается в целенаправленном выборе компонентов, обеспечивающих их совместную работу с эффективной передачей напряжений от волокон к связующему через границу раздела фаз. Прочность адгезионного взаимодействия компонентов при этом может быть выражена через их энергетические характеристики при обеспечении технологических и других факторов. **Цель исследования**: изучение энергетических характеристик фаз гибридного полимерного композита на границе с воздухом. **Методы**: оптическим методом получены микрофотографии смачивания волокон различной природы жидкостями, по которым определены краевые углы смачивания, проведены испытания волокон на растяжение, с использованием синхронного термоанализатора выполнен термический анализ волокон, с использованием тензиометра определены поверхностные натяжения эпоксидной смолы, системы «эпоксидная смола – отвердитель». **Результаты**: Проведена модернизация метода определения поверхностных энергий твердых тел. Модернизированный метод позволяет проводить определение свободной поверхностной энергии волокон различной природы и поверхностного натяжения связующего. Проведена количественная оценка эффекта от замасливающих композиций (аппретов).

Ключевые слова: композит, гибрид, адгезия, смачивание, работа адгезии, свободная поверхностная энергия.