

Aramid Fiber Reinforced Epoxy Composites: Fiber–Matrix Joint

Yu. M. Milyochin^a, S. A. Gusev^a, G. V. Lunkina^a, V. V. Sokolov^a, I. V. Tikhonov^b, and V. M. Shchetinin^b

^a*Soyuz Federal Center for Dual-Use Technologies, Dzerzhinsky, Moscow oblast, 140090 Russia*

^b*LLC Scientific Production Company Termotex, Mytishchi, Moscow oblast, 141009 Russia*

e-mail: skit988@mail.ru

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Abstract—The regularities of intermolecular and chemical interactions of aramid fibers and the epoxide matrix have been studied. The strength of the composite interface has been shown to be determined by the fiber–matrix joint.

Keywords: polymer composite, aramid fiber, adhesion

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INTRODUCTION

Polymer composite materials (PCMs) based on aramid fibers (organoplastics) are widely used to create the articles for different purposes both in domestic industry and abroad. This is due to the high strength of organoplastic combined with a low density. The most widespread initial components for manufacturing of organoplastics in Russia are the Ruser-C, Ruslan, and SVM fibers and EDT-10 epoxide binder. For example, the specific strength (relation of strength to density) of the unidirectional composite based on Ruser-C reinforcing material and EDT-10 resin is much higher than that of carbon plastic analogs (prototypes) based on the best foreign carbon fibers (Table 1).

The strength of the adhesion joint at the fiber–matrix interface plays an important role for the PCM strength properties formation, the uniformity of the stress distribution, and the fracture mechanism that also depends on this characteristic. Adhesion strength is determined by more than just the diffusion of the matrix components into the surface layers of aramid reinforcing materials (RMs), which are studied and described in detail in [1, 2]. The presence of reactive functional groups able for interaction with the matrix on the fiber surface is also an important factor. The

number of the bonds formed as a result of chemical and intermolecular interaction depends on the completeness of the substrate wetting by the resin. Thus, a large number of interconnected processes occur at the RM–resin interface when manufacturing the PCM. The study of these processes will allow the adhesion strength of a composite to be predicted and regulated under different operating conditions.

The aim of the work was to study the regularities of fiber–matrix joint formation when manufacturing of the composite based on aramid fibers and epoxide resin.

EXPERIMENTAL

Kevlar, SVM, Ruser-C, and Ruslan fibers in the form of threads and 2-mm-thick film, obtained by the precipitation of a fiber-forming copolymer (for Ruser-C and Ruslan fibers) in water were used as substrates. The structure formulas of fiber-forming polymers are presented in Fig. 1. EDT-10 epoxy resin was used as a matrix. The resin contains epoxydiane oligomers based on epichlorohydrine and diphenylolpropane of ED-20 grade, diethyleneglycol diglycidyl ester (DEG-1), and amine curing agent triethanolamine titanate (TEAT).

Table 1. Strength characteristics of unidirectional composites based on the reinforcing materials produced domestically and abroad

Type of composite	Organoplastic		Carbon plastic	
	Ruser-C (Russia)	Ruslan (Russia)	T800-NV (Japan)	Tenax (Japan, Germany)
Tensile strength, GPa	2.5	1.9	2.1	2.3
Specific tensile strength, mN m/kg	1.9	1.4	1.3	1.5

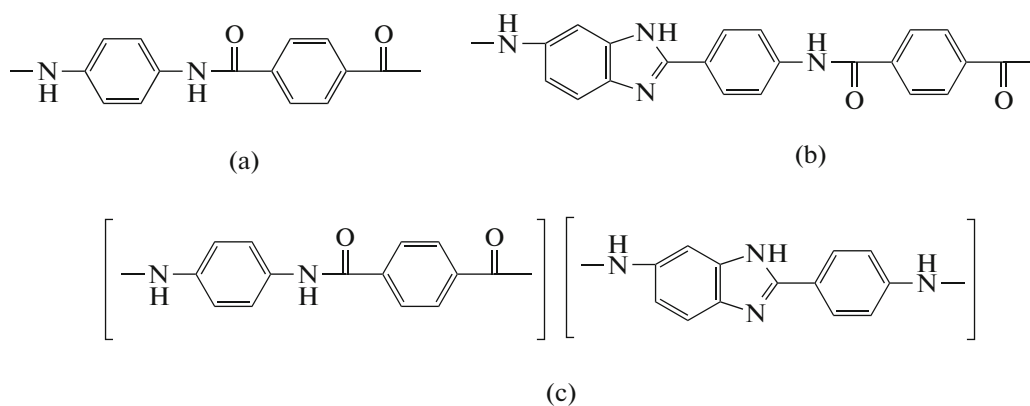


Fig. 1. Structural formulas of fiber that form polymers for aramid RM: (a) Kevlar; (b) SVM; (c) Ruslan and Rusal-C.

Chemical interactions in the fiber–matrix system were studied by IR Fourier spectroscopy using a Nicolet-50 spectrometer within a wave number range of 400–4000 cm⁻¹. Contact angles with substrate surface wetting by liquids were measured by the sitting drop method [3]. Surface tension of the resin was determined by the Wilhelmy plate method.

To determine the RM free surface energy, as well as its polar and dispersive components, the two-liquid method was used [4, 5], where diiodomethane and water were the nonpolar and polar test liquids, respectively. The values of the surface tension for the test liquids are given in Table 2. Dispersive and polar components of free surface energy for the studied aramid fibers were calculated by the two-liquid method. The system of the two equations was solved as follows:

$$\begin{cases} (1 + \cos \theta_{L1})\gamma_{LV(1)} = 2(\gamma_{LV(1)}^d \gamma_{SV}^d)^{1/2} + 2(\gamma_{LV(1)}^p \gamma_{SV}^p)^{1/2}, & (1) \\ (1 + \cos \theta_{L2})\gamma_{LV(2)} = 2(\gamma_{LV(2)}^d \gamma_{SV}^d)^{1/2} + 2(\gamma_{LV(2)}^p \gamma_{SV}^p)^{1/2}, & (2) \end{cases}$$

where θ_{L1} and θ_{L2} is the wetting angle of the fiber surface by the test liquids $\gamma_{LV(1)}, \gamma_{LV(2)}, \gamma_{LV(1)}^d, \gamma_{LV(2)}^d$ are the polar and dispersive components of the surface tension of the test liquids, and $\gamma_{SV}^p, \gamma_{SV}^d$ are the polar and dispersive components of the substrate surface.

The contact angle was determined using a DSA 25E device and surface phenomena were studied using a KRUSS processor tensiometer (Germany).

RESULTS AND DISCUSSION

Due to a high reactivity, epoxide groups can interact with a wide range of chemical compounds, including primary and secondary amines, phenols, anhy-

drides etc. [6–8]. The presence of nitrogen-containing groups in aramid reinforcing material allowed supposing that the fibers and epoxide resins become chemically bonded at PCM interface formation.

For the possibility of chemical reactions between the functional groups of aramid fibers and epoxide resins to be revealed, IR spectroscopy was used. The IR spectrum of the blend containing RM Rusal-C and epoxydiane oligomers ED-20 registered as prepared is presented in Fig. 2.

Figure 3 shows the IR spectrum of the same mixture after heating for 48 h at the curing temperature of the ED-20 resin in the presence of TEAT hardener. The spectra were analyzed and bands at 916 and 971 cm⁻¹ were attributed to vibrations of the epoxide ring, while the absorption bands at 3276 and 1643 cm⁻¹ were assigned to the NH group and amide I of the aramid fiber, respectively.

The data on the integral intensity of the main absorption bands of Rusal-C fiber and ED-20 epoxide resin subjected to heating at 150°C are presented in Table 3.

The intensities of the absorption bands at 3276 and 1643 cm⁻¹ attributed to the NH group of the aramid fiber were shown to be decreased by 30–34% after heating. In addition, the intensities of the bands that

Table 2. Surface tension (γ_{LV}) of test liquids and its dispersive and polar components

Test liquid	$\gamma_{LV},$ mJ/m ²	$\gamma_{LV}^d,$ mJ/m ²	$\gamma_{LV}^p,$ mJ/m ²
Heptane	20.9	20.9	0
Diiodomethane	50.8	50.8	0
Water	72.6	21.8	50.8

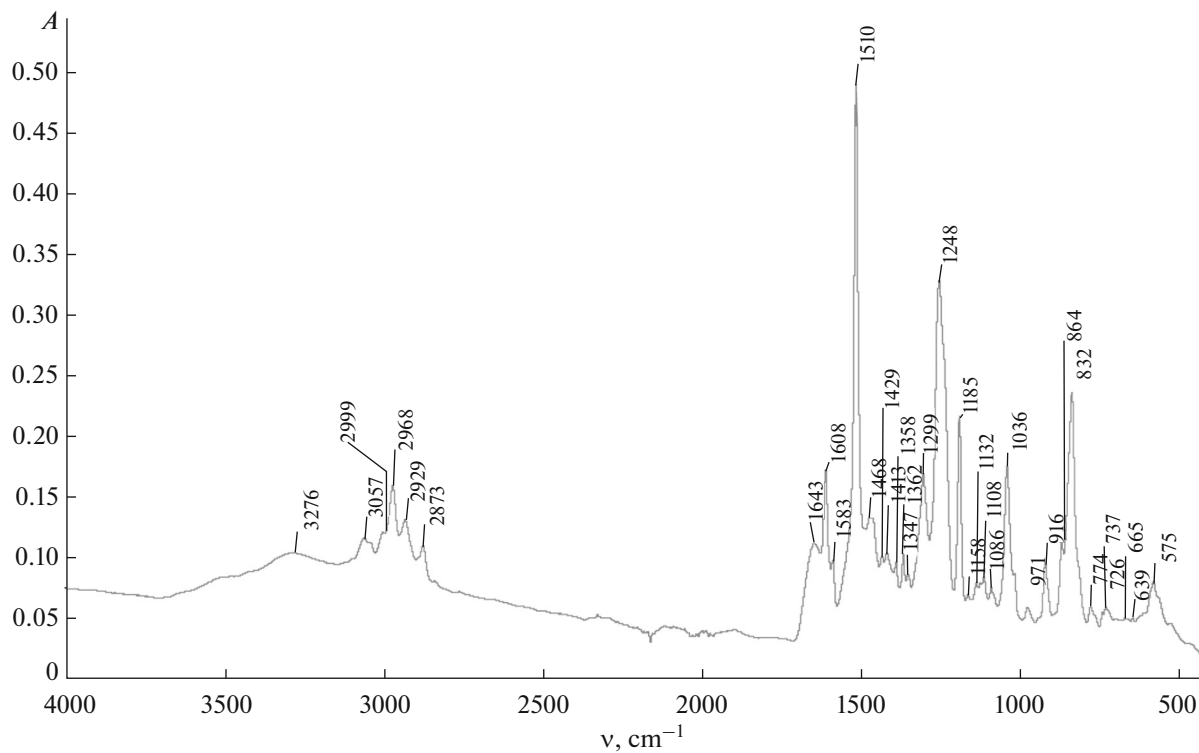


Fig. 2. IR-spectrum of initial Rusar-C fiber–ED-20 resin blend.

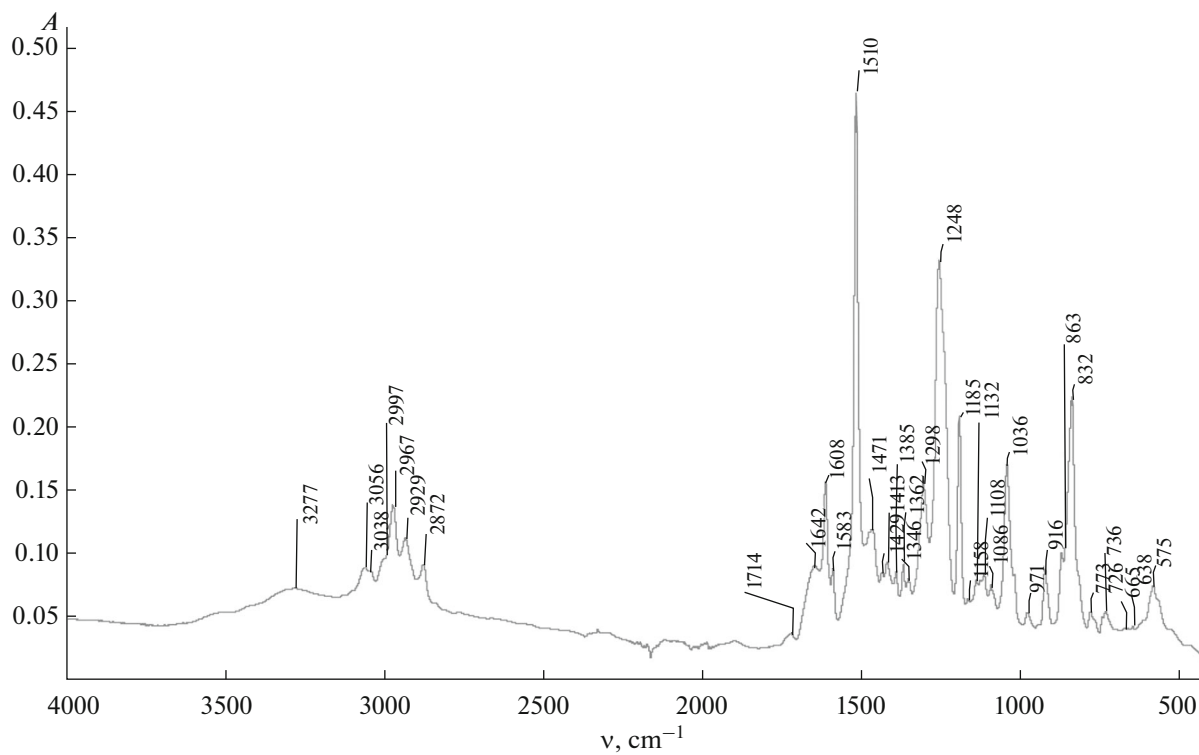


Fig. 3. IR-spectrum of Rusar-C fiber – ED-20 resin blend subjected to heating at 150°C for 48 hr.

Table 3. Integral intensities of characteristic adsorption bands attributed to Rusal-C fiber and ED-20 epoxide resin subjected to heating at 150°C

Heating time, h	Integral intensity of adsorption bands											
	3276 cm ⁻¹ > N–H (fiber)		1714 cm ⁻¹ > C=O carbonyl group (fiber)		1643 cm ⁻¹ – CO–NH–amide I (fiber)		1248 cm ⁻¹ –C–N–		971 cm ⁻¹ epoxy cycle (matrix)		916 cm ⁻¹ epoxy cycle (matrix)	
	value	%	value	%	value	%	value	%	value	%	value	%
Initial	0.354	100	—	0	0.192	100	1.270	100	0.0293	100	0.126	100
16	0.332	93.8	0.027	96	0.171	89.0	1.350	106.3	0.0280	95.6	0.111	88.1
24	0.306	86.4	0.028	100	0.127	66.1	1.390	109.4	0.0270	92.1	0.100	79.4
48	0.245	69.2	0.028	100	0.127	66.1	1.502	118.3	0.0253	86.3	0.100	79.4

correspond to the epoxy cycle of ED-20 resin (971 and 916 cm⁻¹) are decreased by 15–20%. At the same time, the appearance of a new band with a maximum value at 1714 cm⁻¹ is observed, which is explained by the formation of a new chemical bond with the participation of nitrogen of the amide group. The intensity of the absorption band at 1248 cm⁻¹, which corresponds to the formation of a C–N bond, also increases. According to the schemes presented in Fig. 4, these changes in spectral characteristics are typical of reactions between the functional groups of aramid fibers and epoxide resins.

Thus, when curing the composite based on aramid fillers and epoxide resins, the formation of covalent bonds at the fiber–resin interface takes place. The formation of these new bonds, along with intermolecular interactions, results in a high strength of the adhesion joint between the components of an organoplastic.

It should be noted that the content of nitrogen-containing groups in the aramid fiber structure is rather high, i.e., 4.2–4.8 mmol/g. Note that mainly

the groups located on the surface of the threads react with epoxy groups. Thus, the reactivity of aramid fibers in relation to the resins is limited by accessibility of the functional groups and, hence, by the specific surface area of the fiber.

The work of adhesion (W_a), described by the Young–Dupre equation

$$W_a = \gamma_{LV}(1 + \cos \theta), \quad (3)$$

where θ —fiber–matrix contact angle, can be considered to be a quantitative measure of the adhesion strength [9]. As follows from Eq. (3), W_a value is strongly dependent on the real contact area between an adhesive and a substrate, which in turn depends on the free energy characteristic of the contacting phases of the surfaces. The free energy characteristics of the surface for the studied aramid fibers and the film of p-phenylene-terephthalamide and 5(6)-amino-(2-p-aminophenyl)benzimidazole copolymer obtained using the two-liquid technique are given in Table 4. It can be seen that the surface energy value is determined mainly by the dispersive component. The polar com-

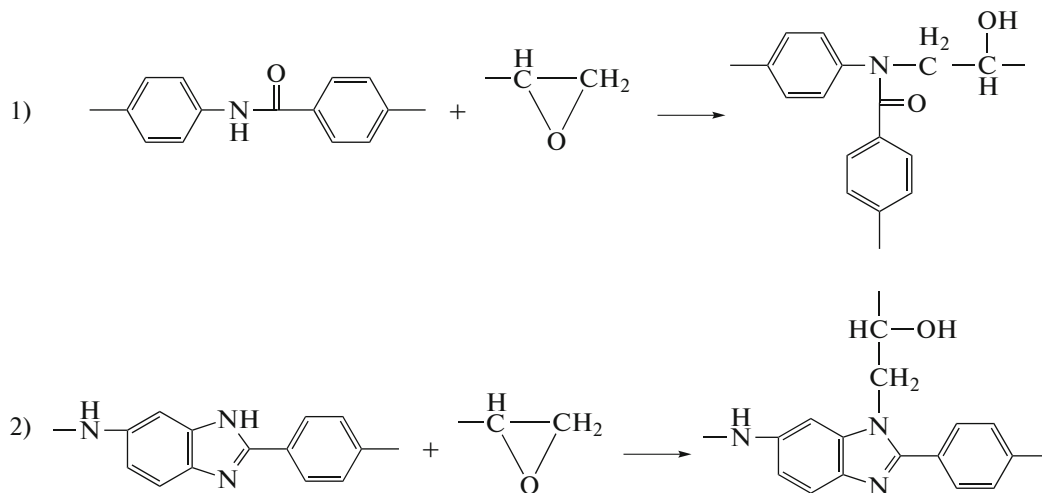

Fig. 4. Schemes of reactions between aramid fiber moieties and EDT-10 resin epoxy groups.

Table 4. Surface energy and its dispersive and polar components for aramid RM and p-phenylene-terephthalamide and 5(6)-amino-(2-p-aminophenyl)benzimidazole copolymer film

Substrate	γ_{SV} , mJ/m ²	γ_{LV}^d , mJ/m ²	γ_{LV}^p , mJ/m ²
Kevlar thread	37	23	14
SVM thread	38	30	8
Rusar-C thread	50	35	15
Ruslan thread	53	37	16
Copolymer film	49	34	15

Table 5. Contact angles of EDT-10 epoxy resin on aramid RM and p-phenylene-terephthalamide and 5(6)-amino-(2-p-aminophenyl)benzimidazole copolymer film after 5–10 s

Substrate	Thread				Copolymer film
	Kevlar	SVM	Ruslan	Rusar-C	
Contact angle, deg.	31	27	19	21	21

ponent in the case of Kevlar, SVM, Ruslan, and Rusar-C fibers is due to the presence of strongly polar amide groups in the structure of fiber-forming polymers.

A neglectable difference in γ_{SV} of chemically identical materials, i.e., Ruslan, Rusar-C fibers, p-phenylene-terephthalamide, and 5(6)-amino-(2-p-aminophenyl)benzimidazole copolymer film, can be explained by the peculiarities of the production method, i.e., by the state of the surfaces.

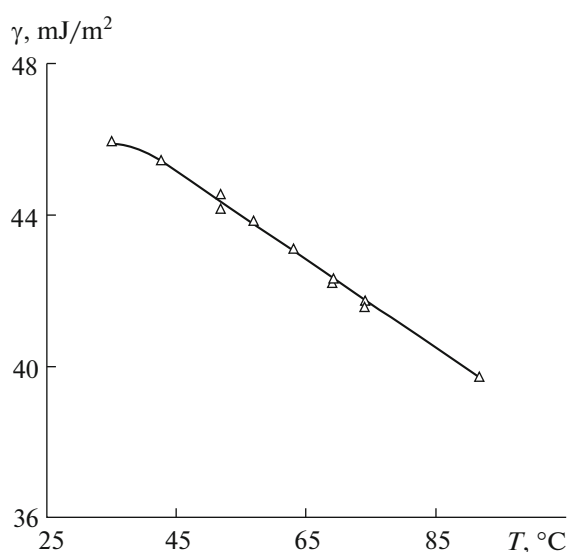


Fig. 5. Surface tension of EDT-10 resin as a function of temperature.

The surface tension of an epoxy resin depends on the processing temperature. The temperature rise results in the weakening of intermolecular bonds and to the decrease of γ_{LV} (Fig. 5).

At a temperature above 40°C, the dependence presented in Fig. 5 was found to be linear, while in a lower temperature range, a deviation from the linear law is observed. This is typical of the associated systems and is likely connected with conformational rearrangements in the oligomer fragments. Nevertheless, in the processing temperature range (60–80°C), variations in EDT-10 surface tension are only 3%. Thus, the contact angle at PCM manufacturing is stable. The values of the contact angle when wetting aramid fibers by the resin measured by the sitting drop method are given in Table 5.

The values of W_a were calculated by Eq. (3) using the data presented in Table 5 and Fig. 5. The work of adhesion for aramid fiber–EDT-10 resin system as a function of the substrate surface energy is shown in Fig. 6. W_a at the fiber–resin interface increases regularly with a rise in γ_{SV} of the aramid fibers due to the increase in the forces of the intermolecular interaction and the contact area of the two phases.

Thus, the fibers arranged in the order of their adhesion to EDT-10 resin will form the following series: Kevlar, SVM, Rusar-C, and Ruslan. The work of adhesion is independent of the method of determination and the conditions of the interface formation so it can be used to estimate the properties of the adhesive joints between aramid fibers and epoxy resins.

The found regularities of chemical and intermolecular interactions between the functional groups of aramid fibers and epoxy resins are intended for use when

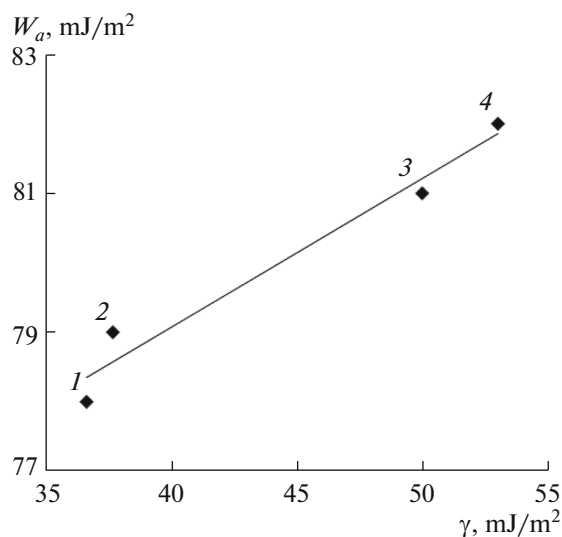


Fig. 6. Work of adhesion for aramid fibers to EDT-10 resin as a function of a substrate surface energy: (1) Kevlar; (2) SVM; (3) Rusar-C; (4) Ruslan.

creating new composites based on the above-mentioned components, the selection of modifying additives for epoxy resins, and the development of modification methods for aramid RM.

CONCLUSIONS

Some regularities for the formation of an adhesion joint between aramid fibers and epoxy resins were established.

Using IR spectroscopy, the curing of organoplastics reinforced by Ruslan-C at $\sim 150^{\circ}\text{C}$ was found to result in the formation of chemical bonds between the functional groups of aramid fibers and epoxy resins. These bonds and intermolecular interactions are responsible for the high strength of adhesion joint between the PCM components.

The surface tension of EDT-10 resin was shown to be stable at the processing temperature range ($60\text{--}80^{\circ}\text{C}$). Thus, the definite contact angle value is observed throughout the PCM manufacturing process.

According to the determined work of adhesion on the organoplastics interface, the fibers arranged in the order of their adhesion to EDT-10 resin were found to form the following series: Kevlar, SVM, Rusar-C, Ruslan.

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