Epoxy Adhesives and Their Application

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Abstract—Characteristics of epoxy film adhesives modified with various rubbers and polysulfone, epoxy adhesive pastes of cold hardening, foaming adhesives, and functional adhesives including conductive adhesives are considered. Advantages of epoxy film adhesives over phenolic-elastomer adhesives are given. Features of adhesion technology with epoxy adhesive and their thermosetting ability providing high strength of adhesive joints of honeycomb structure are given. The fields of application of epoxy adhesives of various types are described.

Keywords: adhesive, film adhesive, conductive adhesive, foaming adhesive, honeycomb structures, honeycomb filler, laminated structures, thermosetting, liners

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Epoxy adhesives are synthetic products that are prepared on the basis of epoxy oligomer and various curing agents of basic or acidic types. The curing process may occur at room and elevated temperatures, depending on the type of curing agent. Epoxy adhesives are widely used in various fields of engineering and economics due to such valuable properties as high adhesion to various materials, high physicomechanical characteristics, marginal shrinkage upon curing, curing without release of side volatile products, high chemical stability, and excellent dielectric characteristics.

Epoxy adhesives possess a number of advantages over phenolic-elastomer adhesives. More specifically:

-they provide higher strength of adhesive joints;

—they do not require the interlayer of liquid adhesive, which results in a significant decrease in the consumption of adhesive per unit adherend surface;

—a significantly lower specific pressure upon gluing; —when gluing honeycomb structures, epoxy adhesives tend to "rise" at the curing temperature along the walls of honeycomb filler and, thus, form fillets around its walls increasing the strength of adhesive joints; owing to this property, the consumption of adhesive is significantly reduced; and

—they are capable of thermosetting, which is used for gluing honeycomb structures with tooling possessing punched holes; in this case, the holes are not filled with adhesive; this characteristic of adhesives was used for the preparation of honeycomb liners [1-3].

VK-31 adhesive was the first film epoxy adhesive. Closed adhesive joints of D16AT aluminum alloy with VK-31 adhesive possessed a shear strength of up to 35 MPa at 20°C, and the joints of honeycomb structure possessed a uniform peeling strength of 6.5-8.5 MPa and a peeling strength of 6 kN/m. It should be noted that fracture of honeycomb specimens occurred on foil at a fracture strength significantly higher than that of phenolic-elastomer adhesives (due to the absence of a punch in the foil) [4]. The curing temperature of $175 \pm 5^{\circ}$ C, at which intercrystallite corrosion may arise in aluminum alloys, is a drawback of VK-31 adhesive; for this reason, work in the field of epoxy film adhesives were carried out for purposes of designing adhesives possessing lower curing temperature (VK-41 adhesive and its counterparts), an increase in their strength characteristics (VK-51 adhesive) and working temperatures (VK-36 adhesives), and a decrease in flammability (VK-46 adhesives) [5–10]. The application of structural epoxy film adhesives is given in Table 1.

Adhesive joints with epoxy film adhesives possess advantages over analogous joints with phenolic-elastomer adhesives not only in initial state, but also after long-term exposure to stress and climatic factors, in particular, in the sea subtropical zone [6]. The combined effect of these factors on the joints of D16AT alloy with VK-32-200 phenolic-elastomer adhesive and VK-31 and VK-41 epoxy film adhesives was studied. The surface was prepared for gluing by anodizing in sulfuring acid with filling of the anode film in potassium dichromate in the case of VK-32-200 adhesive and anodizing in chromic acid in the case of VK-31 and VK-41 adhesives. The load on the specimens was 30% of the initial shear strength. The data showed that the degree of retained strength after exposure of the joints with VK-31 and VK-41 adhesives to sea subtropical conditions and the load is higher than the initial

| • | Adhesive brand | Recommended application | Special properties |
|-----|---|--|---|
| • * | VK-31 | In honeycomb structures from aluminum alloys with nonpunched filler and honeycomb structures from polymer composition materials for gluing tooling with filler | Waterproof high-strength film adhesive. At present, it is replaced by adhesives possessing lower curing tem- perature |
| | VK-36 | In honeycomb structures from aluminum alloys with nonpunched filler and honeycomb structures from polymer composition materials for gluing tooling with filler, as well as metals and nonmetallic materials, in structures operating at temperatures from –130 to +150°C | Possesses high strength characteristics in the recommended temperature range |
| | VK-36A | In honeycomb structures from aluminum alloys with nonpunched filler and honeycomb structures from polymer composition materials for gluing tooling with elements of frame- work | Possesses improved characteristics on gap filling as compared to the VK-36 adhesive |
| , | VK-36R | For gluing nonmetallic honeycomb structures for radiotechnical purposes | Possesses high strength characteristics in the recom- mended temperature range and improved dielectric characteristics |
| | VK-36RM | For gluing structures including honeycomb made from metallic and nonmetallic materials operating in the temperature range from -60 to $+150^{\circ}$ C | Possesses higher strength characteristics in the recom- mended temperature range and decreased curing tem- perature as compared to VK-36R adhesive |
| | VK-36RT.140 VK-36RT.170 VK-36RT.260 | For gluing structures from metallic and nonmetallic materials including honeycomb struc- tures for radiotechnical purposes | Possess high strength characteristics regardless of sur- face density (140–260 g/m ²). Application in honey- comb structures allows one to vary weight characteristics of aggregates |
| | VK-36T | For gluing structures made from metallic and nonmetallic composition materials, honeycomb structures with metallic honeycomb biller, as well as layered structures operating in the temperature range from -60 to $+180^{\circ}$ C | Possesses increased heat resistance up to 180° C as compared to 150 and 160° C of other adhesives of this series |
| - | VK-41M | For gluing of metals and nonmetallic materials in closed adhesive joints, as well as honey- comb structures from aluminum alloys with nonpunched filler and in honeycomb struc- tures from polymer composition materials for gluing of tooling with filler | High-strength adhesive with a decreased curing temperature (125 \pm 5°C) instead of 175 \pm 5°C for adhesives of this series |
| | VK-46B | For gluing of metals and nonmetallic materials in closed adhesive joints, as well as honey- comb structures from aluminum alloys with nonpunched filler and in honeycomb struc- tures from polymer composition materials for gluing of tooling with filler | High-strength nonflammable adhesive |
| | VK-51 | For gluing of structures from metals and polymer composition materials including honey- comb structures from aluminum alloys with nonpunched filler and honeycomb structures from polymer composition materials for gluing of tooling with filler | Possesses high strength characteristics in the recommended temperature range and a high long-term and fatigue strength. The content of volatile substances in the film is $\leq 2\%$, and the mass is $265-325$ g/m ² |
| | VK-51A | For gluing of metals and nonmetallic materials including layered structures, as well as in honeycomb structures from polymer composition materials for connecting tooling with elements of framework | Reinforced with glass fiber and possesses a high long- term and fatigue strength and an increase gap filling ability as compared to VK-51 adhesive |

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| Adhesive brand | Test temperature | Peeling strength of tooling from honeycombs, MPa | | | | |
|----------------|------------------|--|--|--|--|--|
| VK-31 | 80 | 4.4 | | | | |
| VK-36 | 20 | 5.8* | | | | |
| | 150 | 2.4 | | | | |
| VK-41M | 80 | 4.4 | | | | |
| VK-46B | 80 | 3.4 | | | | |
| VK-51 | 20 | 6.5* | | | | |
| | 80 | 5.4 | | | | |
| VKV-2 | 80 | 3.5 | | | | |
| VKV-3 | 150 | 2.5 | | | | |

Table 2. Characteristics of adhesive joints of honeycomb structure with epoxy adhesives

* Fracture by honeycomb filler.

Table 3. Physicomechanical characteristics of epoxy foam adhesives

| Adhesive | | Storage period, | Working | Gluing | | logy | Peeling | Foaming | Apparent |
|----------|---|--|-------------------------------|--|------------|------------------|------------------|-------------|-------------------------------|
| brand | Appearance | rance months/lifetime, tempe h rang | | temperature, °C | time, h | pressure, MPa | strength, MPa | coefficient | density, kg/m ³ |
| VKV-2 | Gray-green film | 6/— | -60+80 | 125 ± 5 | 3 | 0.05 | 3.5 | 1.75-3.5 | 600 |
| VKV-3 | Light-brown to green-brown film | 6/— | -60+150 | 125 ± 5 | 3 | 0.05 | 2.5 (150°C) | 1.45-3.5 | 400 |
| VKV-9 | Homogeneous vis- cous bulk from gray to brown color | -/2 at 18-21°C or -/1 at 30°C | -60+80 | $\begin{array}{c} 18 - 30 \\ 65 \pm 5 \end{array}$ | 24—48 1 | 0.05 | 3.5 | 2-3 | |
| VKV-27 | Homogeneous vis- cous bulk from dark- gray to dark-brown color | -/2-2.5 at 20°C or −/1 at 30°C | -60+80 (protra- ctedly) | $\begin{array}{c} 21 - 30 \\ 65 \pm 5 \end{array}$ | 72 3 | 0.05 | 4.8 | 2–3 | |

* Tests were carried out at 20°C for the specimens: D16AT alloy (anodized) + honeycomb filler from AMg-2N foil (2.5-mm honeycomb).

strength of the VK-32-200 adhesive. After testing under these conditions for 36 months, the decrease in the strength of adhesive joints on the VK-31 adhesive is less than 18%, while the adhesive strength decreased by 25% after 12 months of tests in the case of VK-32-200.

Thus, VK-31 and VK-41 epoxy film adhesives possess high climatic resistance and high working efficiency; in this case, the magnitudes of residual shear strength are nearly two times as large as those of VK-32-200 phenolic-elastomer adhesive.

The need to employ high-strength epoxy adhesives posed the problem of developing new approaches to surface preparation of aluminum alloys for gluing. Surface preparation for gluing with phenolic-elastomer adhesives is performed using sulfuric-acid anodization, which provides high corrosion protection of metal; however, at a strength of the adhesive joint higher than 20 MPa, the anode film is cleaved upon fracture of adhesive joint.

Anodization in chromic acid or phosphoric acid electrolyte is a reasonable approach to gluing with high-strength epoxy adhesives. Epoxy film adhesives are widely used in both closed adhesive joints and honeycomb structures. When there is gluing of honeycomb structures at room temperature, they are fractured along the honeycomb filler. Characteristics of adhesive joints of honeycomb structure are given in Table 2.

Foam adhesives, including film foam adhesives, are used in honeycomb structures along with highstrength adhesive. They are used as joints of honeycomb structures and to mount them to the framework elements. Foam adhesives increase their volume by the factor of 1.5-3.5 upon curing, which allows surfaces with large gaps to be joined. Employment of foam adhesives in joints that do not carry a construction load usually eliminates labor consumption for mechanical treatment of surfaces for gluing, decreases the mass of the adhesive, and simultaneously increases the operational reliability of honeycomb aggregates. Characteristics of foam adhesives are given in part in Table 2 and also in Table 3.

VK-51A adhesive is used in layered structures, in addition to honeycomb structures. Crack growth (if it

| Exposure | Parameter | Initial crack | Exposure period, days | | | | | | | | | | |
|------------|--------------------------|---------------|-----------------------|------|------|------|------|------|------|------|------|------|------|
| conditions | I arameter | length, mm | 1 | 2 | 3 | 4 | 8 | 14 | 28 | 30 | 60 | 90 | 120 |
| ATC | Gain in crack length, mm | 35.2 | 1.6 | 7.9 | 14.9 | 19.5 | 25 | 30.1 | 31.4 | 30.6 | 33.3 | 35.9 | 35.9 |
| | $G_1 \text{ kg/mm}$ | 0.37 | 0.32 | 0.16 | 0.1 | — | 0.05 | | | | | | |
| ASS | Gain in crack length, mm | 31.2 | 1.52 | 2.2 | 5.6 | 14.5 | 20.7 | 24.2 | 31.5 | 34.2 | 51.7 | 9.8 | |
| | G ₁ , kg/mm | 0.55 | _ | _ | 0.32 | 0.14 | — | _ | — | — | — | — | |

Table 4. Crack growth and G_1 for adhesive joints with VK-51A adhesive

 Table 5. Characteristics of epoxy adhesives of cold curing VK-27M and VK-93

| Adhesive brand | after curing a | strength, MPa, at 20°C for 5 h perature, °C | Maximum shear after curing at at test temp | 20°C for 5 h | τ _{shear} , MPa, after thermal aging at 80°C for 1000 h at test temperature of 80°C | | | |
|-------------------|----------------|---|--|--------------|--|--|--|--|
| | 20 | 80 | 20 | 80 | | | | |
| VK-93 | 12.0 | 9.5 | 23.0 | 13.5 | 20.5 | | | |
| VK-27 | 0 | 0 | 24.0* | 10.7 | 13.7* | | | |

* Curing of adhesive joints for 72 h.

arises in the structure) and rate of elastic energy release G_1 are important parameters in gluing. Table 4 shows data on the crack growth and rate of elastic energy release using the "wedge" method after exposure of artificial tropical conditions (ATC) and salt spray (ASS) on adhesive joints with VK-51A adhesive.

A number of structural adhesives of cold curing derived from epoxy oligomers, which are designated for gluing of metals and various nonmetallic materials in adhesive and combined joints (adhesive-riveted, adhesive-welded, and adhesive-threaded), have been developed [11–16]. The first epoxy adhesive of cold curing developed by the All Russian Institute of Aviation Materials was VK-9 adhesive (1983), which has neem widely used in various fields of industry due to its unique characteristics (high strength, no solvent, high rate of curing, and others) and at present is one of the most popular adhesives.

Cured epoxy nonmodified adhesives are brittle and cannot be elongated. To increase their elastic characteristics, they are modified with butadiene-acrylonitrile or other low molecular rubbers. VK-27 adhesive and its modifications are examples of rubber-modified epoxy adhesives of cold curing. VK-27M adhesive, which provides a strength of adhesive joints of D16AT An.Ox.nchr. aluminum alloy of at least 22 MPa at 20°C and 10 MPa at +80°C at shear for 3 days after curing at room temperature is at present the most widespread. The elastic characteristics of VK-27M adhesive (the exfoliation strength) are an order of magnitude higher than those values of the VK-9 adhesive and correspond to 2.0–2.5 kN/m. Adhesive joints can be exposed to $+80^{\circ}$ C for 1000 h without a decrease in strength.

VK-93 epoxy adhesive of cold curing provides a working efficiency of adhesive joints in the temperature range from -60 to $+80^{\circ}$ C, including 80° C, for 1000 h. The adhesive is related to fast-curing adhesives and provides a shear strength of adhesive joints of at least 7 MPa after curing at room temperature for 5 h, which decreases the labor consumption for the gluing process due to the ability to perform subsequent process operations until completion of gluing. Adhesive joints are resistant to water for 5 h at $23 \pm 2^{\circ}$ C; moreover, curing processes continue in water, which is confirmed by an increase in the strength of adhesive joints.

To increase the strain characteristics of epoxy adhesives of cold curing, they are combined with an interlayer of phenolic-elastomer adhesives.

The characteristics of adhesive joints with VK-27M and VK-93 adhesives are given in Table 5.

To increase the thermal stability of epoxy adhesives, they are modified with organoelement compounds. VK-58 adhesive of cold curing is an example of an epoxy-organosilicon adhesive, which operates in the temperature range from -60 to +250°C over a long period and up to 500°C over a short period. The adhesive possesses high process characteristics, and its service life is at least 5 h. The shear strength of adhesive joints of 30KhGSA steel is 14 MPa at 20°C and 0.5 MPa at 500°C.

Conductive adhesives should particularly be mentioned among epoxy adhesives for equipment. Electrically conducting powder fillers are added to epoxy adhesives in order to render them electrically conducting. Powder silver is the most widespread filler. Copper powders are the cheapest fillers possessing low intrinsic resistance; however, due to the fact that they are susceptible to oxidation, it is necessary to protect their surfaces. Carbonyl nickel and carbon powders can be used in conductive adhesives, which do not require high electrical conductivity, as exemplified by equipment to release static electricity in joints [17].

VKP-11 conductive adhesive is dedicated for gluing aluminum alloys, corrosion-resistant steel, brass, and copper with the electrical contact in the structures operating in the temperature range from -60 to $+120^{\circ}$ C. The adhesive does not contain precious metals (it contains carbonyl nickel). Curing of the adhesive occurs at 120°C for 2 h. The shear strength of the adhesive joints is 14 and 4 MPa at 20 and 120°C, respectively, and the bulk electrical resistivity is 4 × $10^{-4} \Omega$ m at the test temperature of 20°C.

A VK-100 one-package epoxy conductive adhesive was developed and now tested as a filler, in which silver powder was used. Adhesive joints with this adhesive possess the shear strength of at least 21 MPa at 20°C and an electrical conductivity less than $1 \times 10^{-6} \Omega$ m at 20°C. The curing temperature of VK-100 adhesive is 175°C.

CONCLUSIONS

Epoxy adhesives are widely used in the machine industry. An incomplete list of epoxy structural adhesives employed in aeronautical engineering indicates the possibility of the solution of important problems using epoxy adhesives.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- E. N. Kablov, "Innovations of the All-Russian Institute of Aviation Materials (VIAM) as part of implementing the Strategic Directions of Development of Materials and Technologies of Their Processing for the Period up to 2030," Aviats. Mater. Tekhnol., No. 1, 3–33 (2015). https://doi.org/10.18577/2071-9140-2015-0-1-3-33
- E. N. Kablov, "Strategic directions of development of materials and technologies of their processing for the period up to 2030," Aviats. Mater. Tekhnol., Suppl., 7– 17 (2012).
- 3. A. P. Petrova and G. V. Malysheva, *Glues, Adhesive Binders, and Adhesive Prepregs* (Vseross. Inst. Aviats. Mater., Moscow, 2017) [in Russian].

- L. A. Dement'eva, L. I. Bocharova, N. F. Lukina, and A. P. Petrova, "Multifunctional epoxy adhesives for aviation technology," Klei. Germetiki. Tekhnol., No. 7, 18–20 (2006).
- N. F. Lukina, L. A. Dement'eva, A. P. Petrova, and A. A. Serezhenkov, "Structural and heat-resistant adhesives," Aviats. Mater. Tekhnol., Suppl., 328–335 (2012).
- A. P. Petrova, N. F. Lukina, and I. A. Sharova, "Assessment of strength of adhesive joints made with epoxy adhesives under the influence of different factors," Polym. Sci., Ser. D 7, 228–232 (2014).
- 7. L. A. Dement'eva, A. P. Petrova, and N. F. Lukina, "Application and function of epoxy film adhesive VK-31," Vse Mater., Entsikl. Sprav., No. 1, 25–29 (2015).
- L. A. Dement'eva, L. I. Bocharova, N. F. Lukina, and A. P. Petrova, "High-strength film adhesives VK-51 and VK-51A," Klei, Germetiki, Tekhnol., No. 4, 17–19 (2015).
- E. N. Kablov, L. V. Chursova, N. F. Lukina, K. E. Kutsevich, E. V. Rubtsova, and A. P. Petrova, "A study of epoxide-polysulfone polymer systems for high-strength adhesives of aviation purpose," Polym. Sci., Ser. D 10, 225–229 (2017).
- A. P. Petrova, L. A. Dement'eva, N. F. Lukina, and L. V. Chursova, "Adhesive binders for polymer composite materials based on coal and glass fillers," Tr. Vseross. Inst. Aviats. Mater., No. 9 (2015). https://doi.org/10/18577/2307-6046-2015-0-9-11-11
- A. P. Petrova and N. F. Lukina, "Foaming adhesives and their application in aircraft construction," Polym. Sci., Ser. D 8, 203–206 (2015).
- N. F. Lukina, A. P. Petrova, R. R. Mukhametov, and A. S. Kogtenkov, "Advances in the field of adhesive materials for aviation purposes," Aviats. Mater. Tekhnol., Suppl., 452–459 (2017). https://doi.org/10.18577/2071-9140-2017-0-S-452-459
- I. A. Sharova and N. F. Lukina, "Gap-filing epoxy cold-setting VK-67M glue," Polym. Sci., Ser. D 5, 282–284 (2012).
- I. A. Sharova and N. F. Lukina, "Fast-curing cold-setting epoxy adhesive VK-93," Klei, Germetiki, Tekhnol., No. 3, 10–15 (2012).
- N. S. Zhadova, T. Yu. Tyumeneva, I. A. Sharova, and N. F. Lukina, "Promising technologies for temporary operational repair of aircraft," Aviats. Mater. Tekhnol., No. 2, 67–70 (2013).
- S. A. Karimova, T. G. Pavlovskaya, and A. P. Petrova, "Surface preparation of aluminum alloys using anodic oxidation," Klei, Germetiki, Tekhnol., No. 1, 34–38 (2014).
- A. P. Petrova, A. Yu. Isaev, N. F. Lukina, K. L. Besednov, and B. F. Pavlyuk, "Fillers for conductive adhesives," Nov. Materialoved., Nauka Tekh., Nos. 5–6, 47–55 (2017).

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