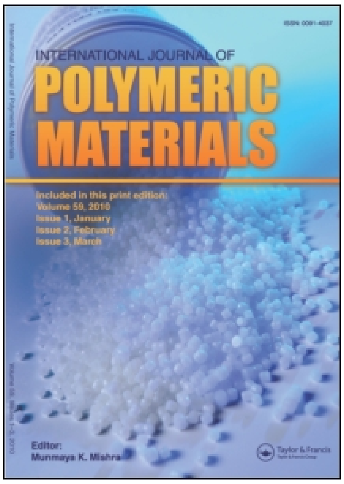

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L. T. Startseva[a]; G. F. Jelesina[b]; O. V. Starstev[c]; G. P. Mashinskaya[a]; B. V. Perov[b]
[a] Department of Physics, Barnaul State Pedagogical University, Barnaul, Altai, Russia [b] VIAM-All-Russian Institute of Aviation Materials, Moscow, Russia [c] Department of Experimental Physics, Altai State University, Barnaul, Altai, Russia

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Effect of Corrosive Medium on Properties of Metal-Plastics Laminates

L. T. STARTSEVA[a], G. F. JELESINA[b], O. V. STARSTEV[c], G. P. MASHINSKAYA[b] and B. V. PEROV[b]

[a]*Department of Physics, Barnaul State Pedagogical University, Barnaul, Altai, Russia;* [b]*VIAM-All-Russian Institute of Aviation Materials, Moscow, Russia;* [c]*Department of Experimental Physics, Altai State University, 66, Dimitrov St., Barnaul, 656099, Altai, Russia*

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The mechanical properties of Alors-laminated pressed systems composed of thin aluminium alloys alternating with layers of organic fiber reinforced plastic has been investigated. The investigation included three main stages. At the first stage, the effect of Alors composition on the fatigue strength, adhesive strength and deformability was studied. The second stage included the shortcut cyclic corrosion tests. It was found that bending loads inhibited corrosion development at polymer metal interface. The third test stage included long term exposure certification tests in a warm damp climate. The effects of true impact of outdoor corrosion environment were determined and Alors properties stability under operating conditions was proven.

Keywords: Laminates; metal; plastics; corrosive medium properties; aircraft

INTRODUCTION

Since the early 80-s, the All-Russian Institute of Aviation Materials has been developing and studying laminated organic metal plastics (LOMP) for aerospace applications. Of particular interest are Alors-laminated pressed systems composed of thin aluminium alloys of types D16, V95, O1420 0.4–2 mm thick alternating with layers of organic fiber reinforced plastics (OFRP) based on clothes of SVM-fiber (oriented polyamidobenzimidazol) and epoxy-type binders and having a monolayer 0.15–0.25 mm thick [1].

Alors have proven to have major advantages over aluminium alloys in terms of fatigue strength. In LOMP the layers of OFRP inhibit the propagation of cracks occurring in the sheets of aluminium alloys and protect the metal against load, abrasive and other impacts.

On long use of Alors, especially under humid climatic conditions, there is a possibility of moisture penetration into the laminated plastic, which can decrease the interlaminar adhesive strength. To illustrate the point, Figure 1 shows the change in interlayer shear strength τ_z of adhesive compounds D16/VK-41/D16 on a 7-year exposure in different climatic zones of the former USSR. In the samples used, VK-41 of the adhesive epoxy polysulfone type and the surface of D 16 aluminium alloy was treated with chromic acid. During the exposure, the samples did not

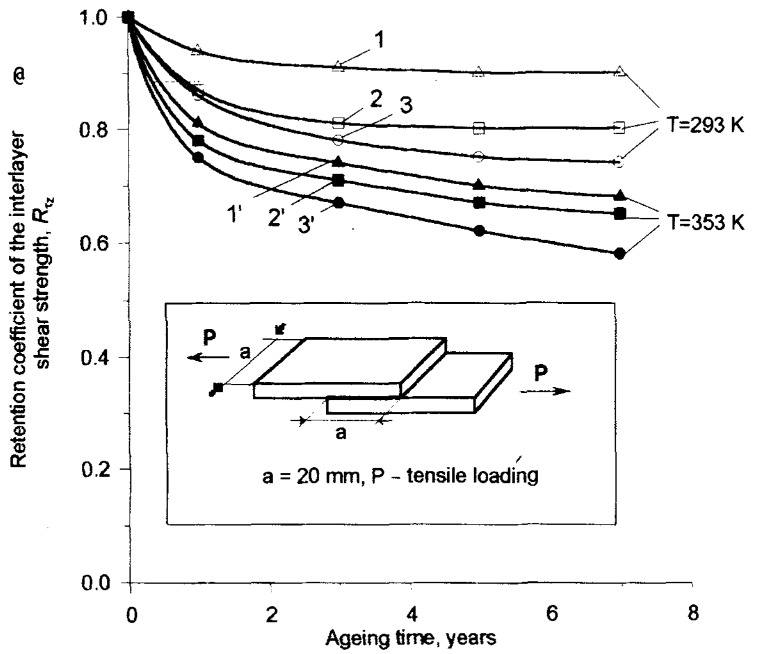

FIGURE 1 Retention coefficient of the interlayer shear strength of VK–41 adhesive τ_z/τ_{z0} (τ_{z0} – for the initial state), measured at different temperatures after a climatic ageing in Batumi (1, 1′), Murmansk (2, 2′) and Zvenigorod (3, 3′) (with the loading scheme in the insert).

have any additional coating to prevent the butt-ends from being affected by the atmospheric moisture. Figure 1 shows how, after 7 years of exposure, τ_z of the adhesive compound decreases, at 293 K, by 10–25%, and at 353 K-by 30–35%. Because of this problem, we decided to investigate in the paper the polymer-metal interface stability. Investigations made in the last ten years included three main stages.

PROPERTIES OF ALORS IN INITIAL STATE

In the first stage we studied the effect of Alors composition on the fatigue and adhesive strength, by varying the types of aluminium alloys, their crystalline structure, the ways of surface protection, thermomechanical "prehistory", etc. Simultaneously with the above-mentioned, the impact of chemical composition of epoxy binders in OFRP and pressing conditions were investigated. The strength of Alors was estimated from the results of testing during the process of cyclic tension of the damage-free specimens and those with the holes simulating the deformation of sheating [1]. The adhesive properties were controlled by change in dynamic shear modulus G' [2] and interlayer shear strength [3].

The properties of Alors based on V95, D16, O1420 aluminium alloys are shown in Table I. The analysis has shown that Alor's strength level surpasses that of aluminium alloys. The use of Alor increases the strength by 12–18%, and by 48% if unidirectional OFRP is used. If the initial crack is formed in the metal layers, strong OFRP prevents the crack opening and reduces the intensity of slow propagation of fatigue cracks. The combination of high fatigue strength and high damping capability in OFRP is the reason for high acoustic endurance of Alors which is 10 times higher than that one of aluminium alloys. OFRP layers in Alor improves the functioning of metal layers at impact loading. OFRP layers, along with the damping, change the nature of metal fracture and localize the area of fracture across the thickness.

The comparison of mechanical properties of Alors with their components was made using the method of dynamic mechanical analysis (DMA) [2] with free damping oscillations. Figures 2, 3 shows the temperature dependences of mechanical loss tangent tgδ and dynamic shear modulus G' of Alor (D16 + Organite 41), D16 aluminium alloy,

TABLE 1 Comparison of properties of aluminium alloys with those of Alors in the initial state

Material	*Content of OFRP* in the package, vol %*	*Tensile strength σ_t, MPa*	*Young modulus E, GPa*	*Number of cycles before fracture** N.10^{-5}*	*Specific strength σ_t/ρ, MPa.m^3/kg*
Sheet of V95 alloy 1.8 mm thick	0	545	72	1.0	0.191
Alor based on sheets of V95 alloy	12	47	67	1.4	0.204
Sheet of D16 alloy 0.44 mm thick	0	415	70	0.4	0.165
Alor based on sheets of D16 alloy	31	510	59	0.4	0.195
	24	430	63	0.6	0.180
	14	430	67	1.2	0.168
Sheet of O1420 alloy 1.08 mm thick	0	444	76	0.9	0.180
Alor based on sheets of O1420 alloy	17	478	72	1.1	0.212

* OFRP = SVM + VK – 41 (Organite 41)
** for a strip with in the process of pulse extension at the maximum stress of a cycle of 160 MPa at the frequency of 3 Hz

OFRP of Organite 41 (SVM + VK–41) type, separately hardened binder VK–41, adhesive compound (D16 + VK–41). The nature of temperature dependences $G'(T)$ and $\mathrm{tg}\delta(T)$ reflect the properties of its individual components. For instance, α-peak of $\mathrm{tg}\delta$ at 340–370 K which is the glass transition region of VK–41 binder, is prominent also as a part of OFRP and as a part of Alor. Similarly, α'-peak of $\mathrm{tg}\delta$ at 520–550 K, which is the glass transition region of SVM fiber, also exists in OFRP and Alor (Fig. 2).

The drop in G' in the region of α-transition of VK–41 binder (Fig. 3) is notable in OFRP, adhesive compound, and Alor. The $\mathrm{tg}\delta$ value of Alor is calculated by the additivity law for non-interacting mix

$$\mathrm{tg}\delta = \mathrm{tg}\delta_{\mathrm{SVM}}\varphi_{\mathrm{SVM}} + \mathrm{tg}\delta_{\mathrm{VK-41}}\varphi_{\mathrm{VK-41}} + \mathrm{tg}\delta_{V95}\varphi_{V95}, \tag{1}$$

at $\varphi_{\mathrm{SVM}} + \varphi_{\mathrm{VK-41}} + \varphi_{V95} = 1$ for volume parts of Alor components. The value of Alor's G' is described by the ratio

$$G' = G'\frac{1 + AB\varphi_2}{1 - B\Psi\varphi_2}, \tag{2}$$

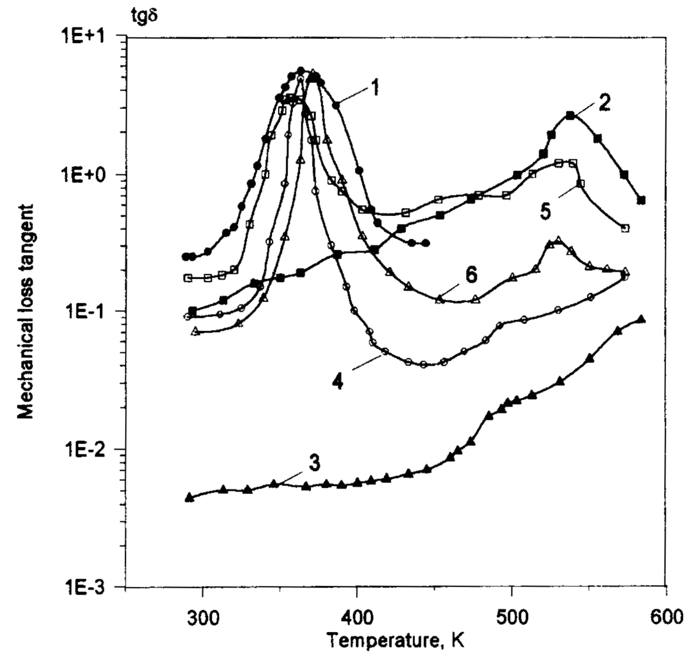

FIGURE 2 Comparison of temperature dependences of mechanical loss tangent of Alor's and its components: 1–VK–41 binder, 2–SVM fiber, 3–D16 aluminium alloy, 4–adhesive compound D16 + VK–41, 5–Organite 41 (SVM + VK–41), 6–Alor (D16 + Organite 41).

where G'_1 is the dynamic shear modulus of Organite 41, A, B, Ψ are constants. The values of G' and tgδ, and the temperature half-width of α-peak of tgδ are quite sensitive to the variation of composition, pressing regimes, methods of treatment of aluminium alloy surface, etc.

PROPERTIES OF ALORS AFTER SHORTCUT CYCLIC CORROSION TESTS

The second stage of the research included the shortcut cyclic test of Alors. The overall duration of the cycle was 1 hour. During the test, for 10 minutes, moistened with electrolyte (distilled water, sea water, 3% NaCl solution) and then kept in the air at room temperature for 50

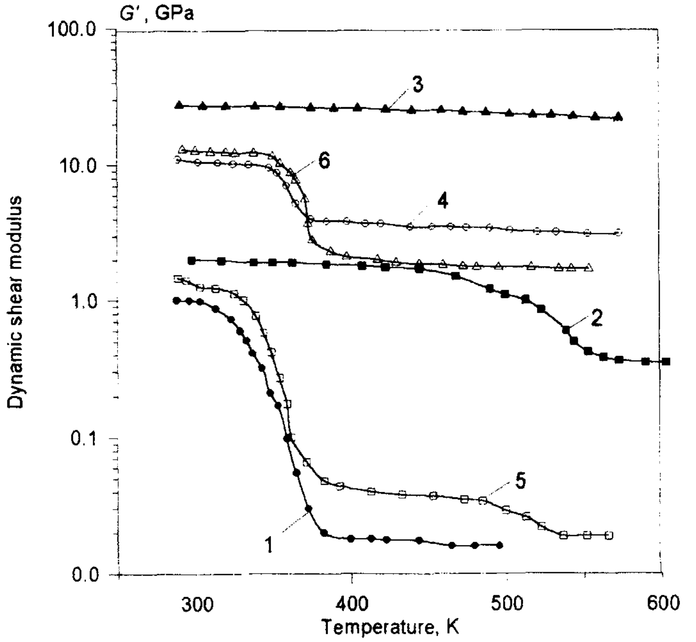

FIGURE 3 Comparison of temperature dependences of dynamic shear modulus of Alor and its components. Symbols are the same as in Figure 2.

minutes. Alors properties parameters were measured after 720, 1440, 2160 and 2880 cycles. At this stage, the composition, processing technology of metal surface protection were optimized with respect to polymermetal interface corrosion stability. The specimens were tested in a stress free state and under three levels of static bending loads. The medium effect was estimated by sorbed water quality, swelling, corrosion development using metal-graphic analysis, and also by change in deformability and interlaminar strength.

Figure 4 shows the kinetics of water sorption w and change in thickness h-h_0/h_0 of Alor specimen at the cyclic tests. The largest changes of these parameters were recorded for unprotected by coatings samples in NaCl solution. Notable changes in Alors properties take place after 60 days of experiments. After 120 days $w = 10.5 \pm 0.5\%$, $\Delta h/h_0 = 30\%$. This negative effect is less prominent at the contact with sea salt water. Varnish and paint coating fully prevent Alor from aggress environmental impact.

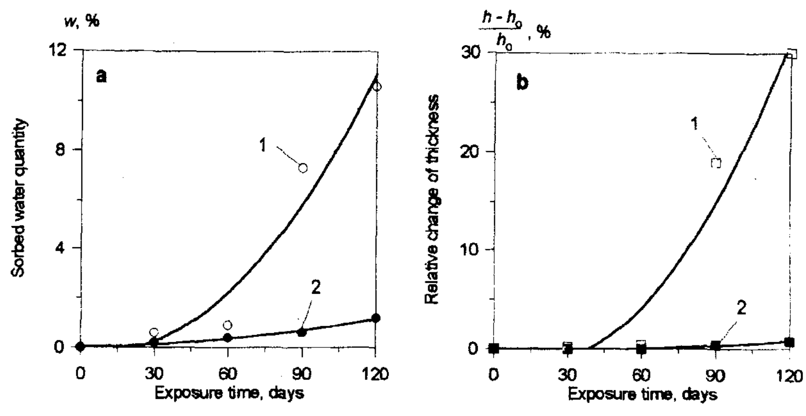

FIGURE 4 Influence of the duration of Alor's ageing in corrosive active media on the quantity of the sorbed water (a) and the change in thickness of Alor's samples (b), 1–exposition in 3%-solution of NaCl, 2-exposition in sea water.

Figure 5 shows the influence of exposure in NaCl solution on temperature dependence G' of unprotected specimens exposed without loading. It has turned out that, at room temperature, G' linearly decreases as w increases.

$$G' = G'_0(1 - k_1 w), \tag{3}$$

where G'_0 is dynamic shear modulus in the initial state, $k_1 = 2.92$. Plastification effect of water on VK–41 binder as a part of Alor is described by the glass transition temperature $T_g(w)$ [2] dependence

$$dT_g/dw = -k_2(T_g - T_{gm}) \tag{4}$$

with limiting conditions of $T_g = T_{g0} = 367\ K$ at $w = 0$, $T_g = T_{gm} = 352$ K and $dT_g/dw = 0$ at w_m, where w_m is the maximum quantity of sorbed water.

The most interesting and the most important result is in discovering that applying the mechanical bending load $\sigma_b = 130$ MPa significantly slows down negative environmental impact on Alor. Change in G' for

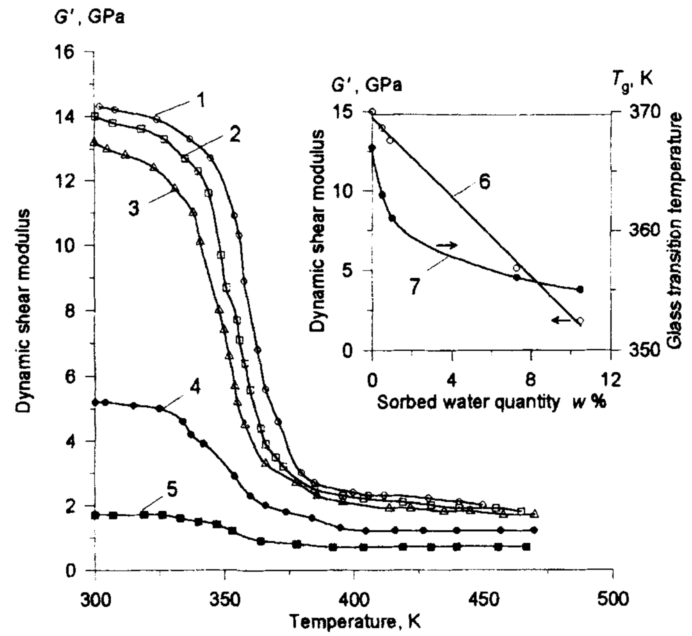

FIGURE 5 Temperature dependences G' of Alor in the initial state (1) and after the cyclic tests in 3%-solution of NaCl, for 30 days (2), 60 days (3), 90 days (4), and 120 days (5). In the insert: dependences G' at 293 K of Alor (6) and glass transition temperature of VK – 41 binder as a part of Alor (7) on sorbed water quantity.

unprotected specimens under the bending loads during the 120 days of cyclic tests in NaCl solution did not surpass 10%. For Alor (D16 + Organite 41) of yet another lot where plates of D16 alloy with the surface untreated were used, the best result was obtained for the bending load of 80 MPa (Tab. II).

The analysis of the specimens' interlayer fracture after the corrosion tests has shown that the nature of destruction changes from cohesive to adhesive as the corrosion damages occur on the surface of aluminum alloy when in contact with OFRP. Thus, it is proven that decrease in G' of Alor is caused by the metal's interlayer corrosion that develops under the influence of sea water sorbed by OFRP from the environment. Mechanical stresses in OFRP slow down the diffusion processes in moisture and increase Alor's stability to environment.

TABLE II Influence of the bending load level on dynamic shear modulus retention coefficient for Alor (D16 + Organite 41) with untreated surface of D 16 sheets

Time of exposure,	$R_{G'} = G'/G_0^*$			
days	$\sigma_b = 0$	$\sigma_b = 80\ MPa$	$\sigma_b = 100\ MPa$	$\sigma_b = 130\ MPa$
30	0.86	0.97	0.95	0.95
60	0.69	0.86	0.78	0.78
90	0.23	0.45	0.34	0.30
120	0.05	0.26	0.15	0.10

* $G_0 = 14.3$ GPa

PROPERTIES OF ALORS AFTER EXPOSURE IN A WARM DAMP CLIMATE

The third test stage included long term certification tests. For this purpose, plates or strips of Alors without protection or protected by paint coatings were exposed in a free state or under the impact of bending and tensile loads for 5 years under the conditions of a humid subtropical climate. From the results of these tests (Tab. III), the effects of true impact of outdoor corrosion environment were determined and Alors properties stability under operating condition was proven.

TABLE III Influence of 5-year exposure in a warm damp climate on Alor's mechanical properties

Conditions of exposure	*Tensile strength* σ_t*, GPa*	*Young modulus E, GPa*	*Interlayer shear strength* τ_z*, MPa*	*Dynamic shear modulus G', GPa*
Initial state	0.395	57.5	21.5	12.5
Open atmospheric stand without loads	0.395	57.5	21.0	12.0
Shed without loads	0.395	57.5	20.5	11.5
Open atmospheric stand with the bending load of $\sigma_b = 100$ MPa	0.405	57.5	20.0	12.5
Open atmospheric stand with the bending load of $\sigma_b = 130$ MPa	0.405	57.0	20.0	12.5

CONCLUSION

The requirements for Alor to avoid corrosion processes and reduction in the interlaminar strength were improved. The results of analysis and data quantitative processing after shortcut and environmental tests, which are given in the paper, allow to predict operating capacity of aircraft carrying sheathings and include concrete recommendations for optimizing the properties of LOMP at the stanges of technology, design and operation.

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