MOISTURE RESISTANCE OF NEW GLASS/EPOXY-ALUMINIUM LAMINATES

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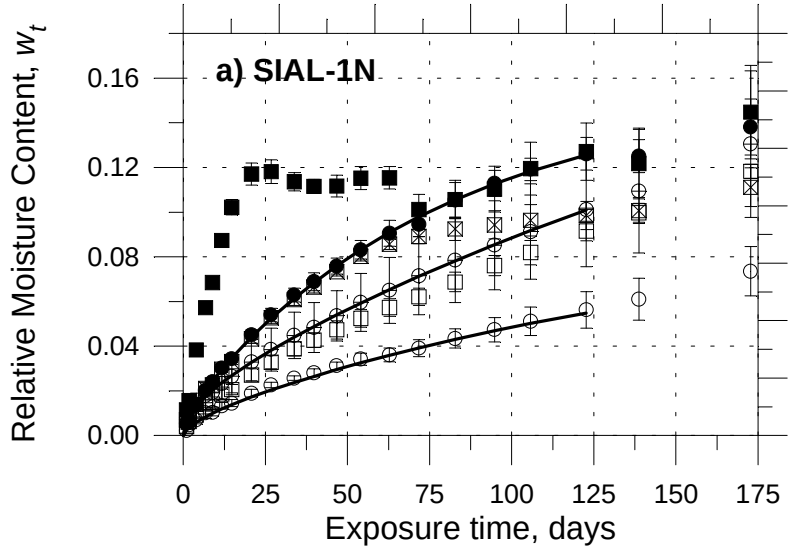
In 80 years the All-Russian institute of aviation materials has developed hybrid composite materials (ALOR) on a base of organic fiber reinforced plastics (OFRP) and aluminum alloys for application in structural primary elements of flying devices (skins, stoppers, etc.).

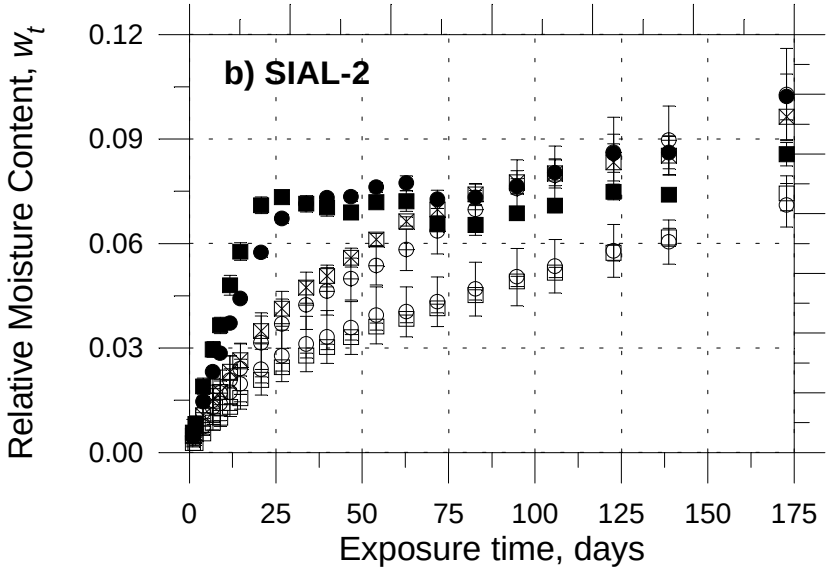
ALOR shows superior advantages as compared to aluminum alloys at long cyclic loading. In ALOR layers of organic fibers strengthen a matrix, interfere with distribution of cracks appearing in aluminum alloys sheets. However, during exposure of ALOR in a warm damp climate there is an opportunity of water penetration in volume of a matrix, that is why dynamic rigidity C', glass transition temperature T_g are lowered. Corrosion develops on polymer/metal interface in these conditions [1]. The glass fiber reinforced plastics (GFRP) (high strength glass reinforced materials) are applied for correction of this lack in new metal-composite instead of OFRP, having smaller sorption capacity and also for increasing static tensile and compressive strength and for decreasing prize and availability of materials [2]. New SIAL laminate on the base of GFRP have been developed.

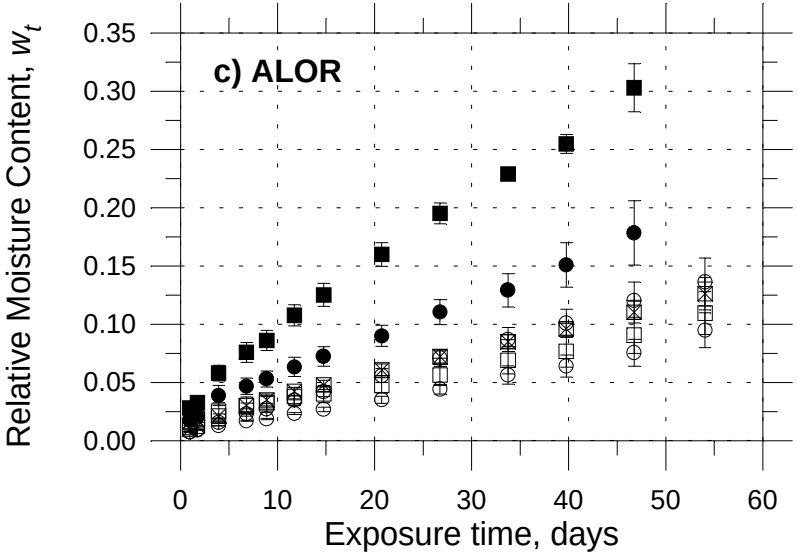
There were carried out extensive experiment on humidifying ALOR and SIAL samples of the various form and sizes in identical conditions (temperature ~60°C, relative humidity ~100 %). The sorption was examined within 150 day in stationary conditions. At the analysis of results it was taken into account, that the moisture was distributed in volume of a polymeric composite. The experiment has confirmed advantage of GFRP to influence of moisture in comparison with OFRP in layered systems. After 40 day ALOR have begun partially to be delaminated, and were completely stratified after 50 day. The absence of continuous adhesion connection between a polymeric matrix and metal was the reason of similar behavior. In formed delamination emptiness water will penetrate, that results in corrosion of an aluminum alloy and, as a consequence, complication of sorption process: on border undressed polymer/metal interface there are additional sorption areas of water. At the same time any SIAL damages was not revealed during 120 day humidifying, though the characteristic profile of a sorption curve was shown, that water diffusives by not Fick's low in this case (Fig. 1).

For all types of metal-composite the tendency to unequal limiting moisture saturation by samples of the different sizes is found out. The presence of edge (1), formed at cutting of samples, is the most probable reason of such effect. The influence of edge sharply grows for samples of the small sizes

$$w = w_0 + V_k\left(w_k - w_0\right); \qquad V_k = \frac{2}{ab}\left(ad_1 + bd_2 - 2d_1d_2\right), \tag{1}$$







	Length * Width
Along of reinforcing direction :	100 * 50 mm^2
	100 * 25 mm^2
	100 * 10 mm^2
Cross of reinforcing direction :	100 * 50 mm^2
	100 * 25 mm^2
	100 * 10 mm^2

Fick's law with relaxation (3)

Figure 1. Sorption curves of glass/epoxy-aluminum laminates at T = 60°C and relative humidity 100%

where w is common moisture content; w_k is moisture content in damaged edge; w_o is moisture content in volume; V_k is volumetric share of edge; L is length of a sample, sm; H is width of a sample, sm; d_1, d_2 are depths of damaged edge, various for two directions (Fig. 2).

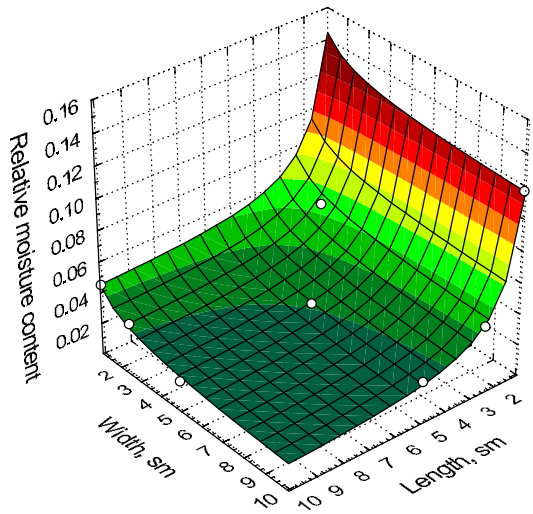


Figure 2. Damaged edge of SIAL

The conducted experiment has detected an anisotropy of sorption properties of a material. The samples with the greater square of a lateral area swallow water with the greater velocity, it is proved to a comparison of factors of declination of sorption curves, which are connected to an effective diffusivity proceeding from models, where the stream through a lateral area is substituted by an one-dimensional stream along effective direction of a diffusion. In this case it is possible to determine a product of a diffusivity on limiting moisture content in a unit of length of a diffusion path under the formula [3]

$$\frac{D \cdot w_{\infty}}{h} = \frac{\pi}{4}\theta \ , \qquad (2)$$

where D is diffusivity from the one-dimensional Fick's law [4]; w_{∞} is limiting moisture content in a sample from the equation (1); h is effective length of a diffusion path; θ is tangent of an angle of sorption curve declination on an moisture content's dependence from the radical square of time of humidifying on a part of time, where declination is constant (tab. 1).

Table 1

Growth rate of moisture content of glass/epoxy- aluminum laminates θ, (sm/days) (2)

Sample's width *, sm	ALOR		SIAL-1N		SIAL-2	
	Along**	cross**	Along**	Cross**	along**	cross**
1	0.020	0.038	0.013	0.032	0.018	0.020
2,5	0.010	0.014	0.009	0.0125	0.008	0.010
5	0.005	0.008	0.005	0.009	0.005	0.0055

* – Sample's length is 10 sm

** – Along and cross of the basic reinforcement

Difference of growth rate of moisture content of the material with the different form is explained by availability of the sample's damaged edge. There is the microcracks' distribution, which is derivated after cutting. Tests of samples with identical square but different orientation have confirmed availability of an anisotropy of depth of a penetration of microcracks in a matrix.

The apparent completion of moisture content on SIAL-1N and SIAL-2 samples with sizes 10×1 sm^2, especially across of reinforcement of filaments is explained by a sum of two processes – penetration of water in glass fiber reinforced plastics and oxidation of aluminum with selection a settling on surface of samples. The sediment is deleted before weighing.

The fig. 1 illustrates modeling of sorption curves by anomalous Fick's law (Case II) with varying of the boundary condition [5,6]

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2}\ ,\quad c_G = c_\infty + (c_0 - c_\infty)e^{-dt}\ , \tag{3}$$

where c is concentration of water; $c_G(t)$ is time-dependent concentration on the boundary; c_0 is initial distribution of water on the boundary; c_∞ is distribution of water for want of t seek to infinity; t is time, day; x is the coordinate, along which water diffuses; D is diffusivity, sm^2/days; d is relaxation rate, 1/days.

The reason of a relaxation is the modification of free volume and, as a corollary, magnification of a sorption capacity, and also sorption dependence of a diffusivity. Moisture content in volume of a sample in case when the edge effects can be neglected is shown in tab. 2.

Table 2

The upper evaluation of a relative increment of a mass in volume, %

Time, days	ALOR	SIAL-1N	SIAL-2
21	2	1	0.8
46	6	2.4	2
123	–	5	4.5

During tests the temperature dependencies of dynamic shear rigidity C' of initial dry samples unidirectional SIAL for long and transverse directions of a clipping both similar moisture saturated and repeatedly dried up samples were measured. The effect of decrease C' is similar to earlier measured for ALOR [1]. The characteristic of plasticization effect of adhesive by a absorbed moisture, temperature derivative dC'/dT and them spectroscopic decomposition on gaussians (4) for transition binding from glassy to viscoelastic state was used as follows

$$\frac{dC'(T)}{dT} = \sum_{j=1}^{m} a_j \exp\left[-\ln(2.0)\frac{(b_j - T)^2}{d_j^2}\right] \tag{4}$$

where C' is dynamic rigidity; a_j is intensity of peak; b_j is place of the peak center on an axis of temperatures; d_j is half of peak width; T is temperature; m is amount of peaks.

After 123 days in a humid medium at the temperature of 60°C the ALOR samples by sizes 100×10 mm^2 practically have reached maximum in these conditions of moisture saturation. For want of it relative moisture content (in recalculation on a mass of glass fiber reinforced

plastics) has made in SIAL-1N 11 % for the samples cut out across of basic reinforcement and 13 % for the samples cut out along of basic reinforcement. The relative moisture content has made, accordingly, 7 % and 8 % for SIAL-2. It was of interest to define a degree of plasticization effect of a moisture on these materials on a technique, before was used for ALOR [7]. For a measurement of viscouselastic characteristics of a material (fig. 3) the inverse torsion pendulum [8] was used.

Two characteristic attributes prove presence of plasticization influence of a moisture. At first, in samples containing a moisture, dynamic rigidity appreciably decreases. Secondly, glass transition temperature of binding in SIAL is significantly lowered. There was observed characteristic for epoxy matrices [1] division into two areas of glass transition adhesive macrochains in the disorder matrix (66-74°C) and in more ordered sites (88-102°C) while in an initial status unique glass transition temperature was fixed at 124°C. The degree of plasticization action of a moisture on binding of this material is easily defined by comparison of the dynamic rigidity values of dry and moisture saturated samples and displacement of glass transition temperature. After repeated drying the partial recovery of the initial characteristics is observed, that shows relative convertibility of influence of temperature and moisture on mechanical properties of a material (tab. 3).

Table 3

	SIAL-1N (100×10 mm^2)						SIAL-2 (100×10 mm^2)					
	Along			cross			Along			cross		
	init**	Wet***	dry**	init	wet	dry	init	wet	dry	init	wet	dry
C'*, GPa	22	6.2	18	24	6.6	15	16	5.3	11.4	14.5	5.2	11
Tmin, °C	123	68; 88	114	123	74; 102	116	114	62; 92	106	112	65; 100	109

* at T = 25°C
**init – initial dryed; wet – after 200 days of moisturing; dry – after 180 days of repeated drying

The analysis of results of experiment has allowed to receive mathematical model of sorption and diffusion of a moisture in ALOR and SIAL laminates, and also to estimate a degree maximal plasticization effect on SIAL adhesive under operating conditions, as absorption at 60°C simulates the heat at long parking or storage of planes in damp tropics. It is important to note thus, that the investigated samples even after dynamic mechanical measurements have kept the integrity and have not found out attributes of delamination from thermal moisture influence.

CONCLUSIONS

It is possible to select three zones in a time dependence of the moisturing by SIAL: a) the initial filling of volume in basic at the expense of a damaged edge (is observed an dependence on an initial part from sizes and direction of a sample's reinforcement); b) moisture content lowering of a material in an outcome of a course of a chemical response; c) a further raise of moisture content at the expense of developing in a sorption course of an aluminum alloy's corrosion (new sorption surfaces have been occurring). Especially well this gradation is appreciable on samples cross reinforcement with linear sizes (100*10 mm^2).

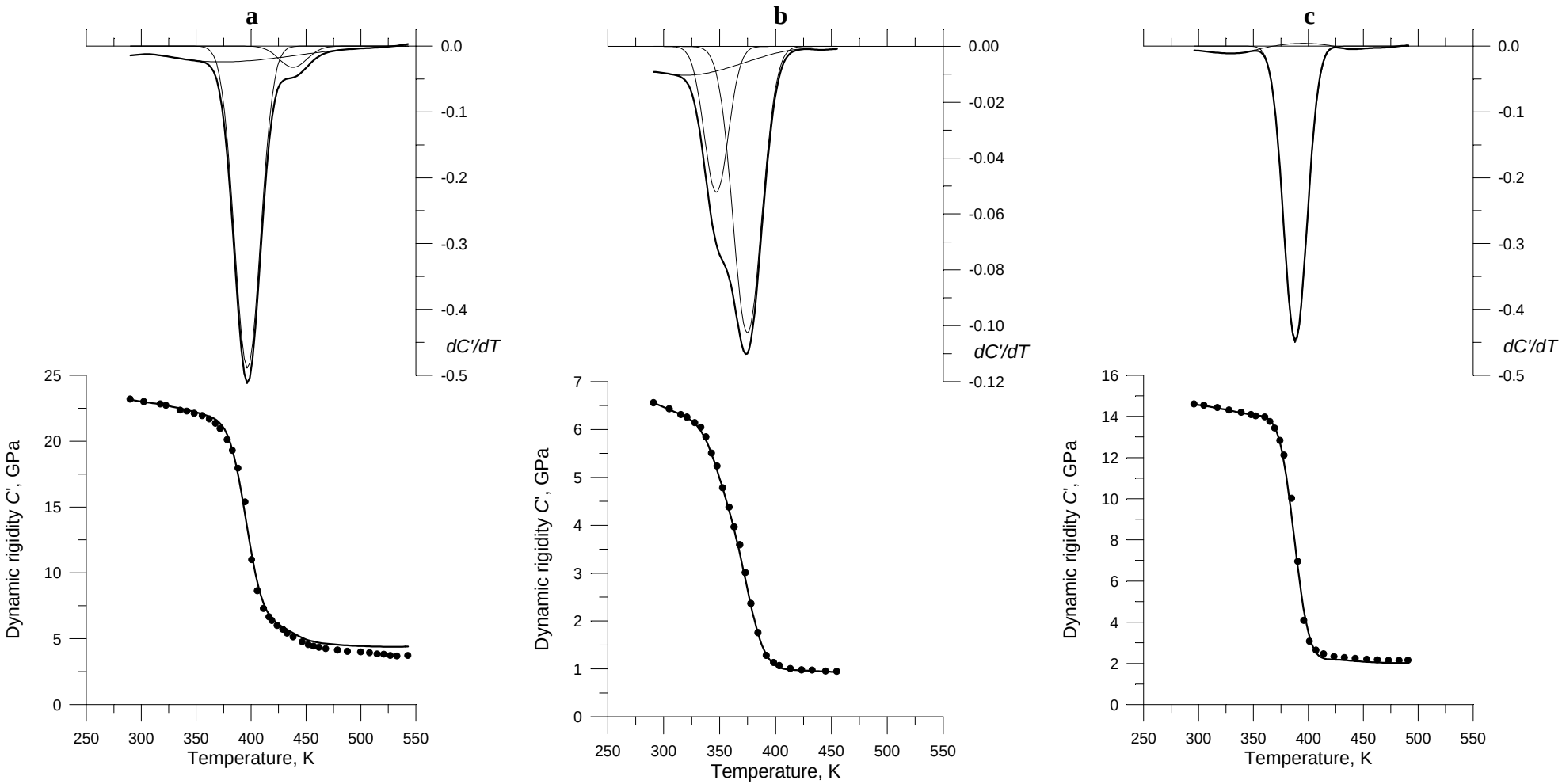


Figure 3. Temperature dependencies of dynamic rigidity (SIAL-1N, 100x10 mm^2, cross direction) a: initial state; b: after moisturing; c: after drying

The dynamic rotating rigidity of SIAL decreases at humidifying. Temperature of a maximum falling of a rigidity displaces in a leg of lower temperatures. The rigidity and temperature of relaxation transition are again increased after repeated drying, but do not reach initial values because of presence of a part of a moisture. The enumerated effects confirm an plasticization operation of a moisture on binding of SIAL.

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