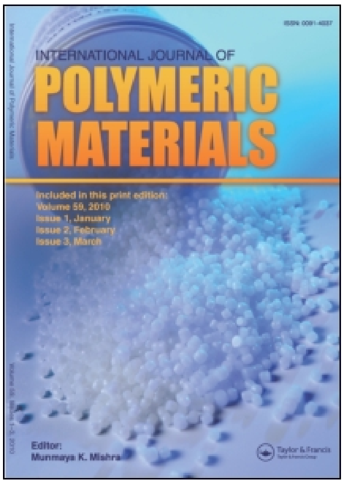

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Interlayer Shear Strength of Polymeric Composite Materials During Long Term Climatic Ageing

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Polymeric composite materials of aviation application based on carbon, organic, glass fibers and epoxy binders were exposed for 10 years under warm humid climatic conditions of the city of Batumi on the Black Sea Coast. In the process of the exposure interlayer shear strength was measured, which was compared with other mechanical and physical characteristics measured in the center and surface layers of exposed plates. It has been shown that the surface of composites exposed to solar radiation is destroyed and disrupted to a greater extent than the inner layers. The gradient of mechanical properties across the thickness of a specimen can be significant. To illustrate the effect, a diffusion model of defects for polymeric composite materials was examined.

Keywords: Climatic ageing; interlayer shear strength; moisture diffusion

INTRODUCTION

Standard methods for determining the strain–stress properties of polymeric composite materials (PCM) exposed to long term climatic ageing have a grave disadvantage. The change of these characteristics across the thickness of specimens is not taken into account when determining shear strength and Young modulus. Mean while it has been known that the surface of PCM exposed to solar radiation is destroyed and disrupted to a greater extent than the inner layers [1].

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*Corresponding author.

On long term exposure of PCM under true climatic conditions the gradient of mechanical properties across the thickness of a specimen can be significant. Therefore, the values of mechanical characteristics of climatically aged specimens determined by standard methods are "effective" characteristics of sorts due to the availability of the properties gradient across the thickness. The use of these "effective" indicators of mechanical strength makes the evaluation of the climatic resistance of PCM of various thickness ambiguous and substantially hampers the prediction of their properties.

To illustrate the importance of the problem, the present paper shows the regularities of the effect of the long-term exposure in climatic conditions of the properties of PCM in aviation application, cites experimental evidence for the existence of the gradient of properties across the thickness of climatically aged specimens and a variant of the model for the quantitative description of effects, has been advanced.

EXPERIMENTAL

PCM of aviation application based on carbon, organic and glass fibers and epoxy binders were exposed for 10 years under warm humid climatic conditions of the city of Batumi on the Black Sea Coast. In the process of the exposure interlayer shear strength τ_z was measured by the procedure [2], which was compared with other mechanical and physical characteristics measured in the center and surface layers of exposed plates.

During the process of exposure standard mechanical characteristics (tensile strength σ_t, bending strength σ_b, compression strength σ_{-t}, tensile fatigue strength σ_{-1}, Young modulus E, shear modulus G', *etc.*) were determined. Physical thermal methods such as dynamic mechanical analysis (DMA), linear dilatometry (LD) and moisture diffusion analysis (MDA) were found to be the most informative and efficient [3, 4]. In our experiments tensile fatigue σ_{-1} was determined by stretching the specimens with the zero cycle with the loading frequency of 25 Hz on the basis of 10^7 cycles. Testing of specimens started from the top levees of loading which were selected in such a way that the operating mean-time constituted $10^3 - 10^4$ cycles, the intervals of lowering the levels were selected in such a way that the operating time on the subsequent level did not exceed one decimal place. The level of loading on which one or two specimens were run through a basic number of cycles without breaking, was taken to be $1.1 \cdot \sigma_{-1}$ or $1.05 \cdot \sigma_{-1}$. As a check upon the identification of the expected tensile fatigue strength in the indicated range of tension, was the testing of 5 specimens on the $0.9 \cdot \sigma_{-1} - 0.95 \cdot \sigma_{-1}$ level.

To estimate the value of the gradient of properties across the thickness of PCM, the method of measuring the interlayer strength τ_z[1] was employed. Figure 1 shows the specimen and the diagram of the device eliminating the bending error. Therefore, the technique is profitably employed to measure τ_z at different depths in PCM specimens after prolonged climatic ageing.

RESULTS AND DISCUSSION

The effect of a warm damp climate on the mechanical parameters of composites after a long-term real exposure can be estimated from the generalized data [1] listed in Table I [3].

By monitoring the mechanical indicators of PCM depending on the time of exposure under climatic conditions, it has been established

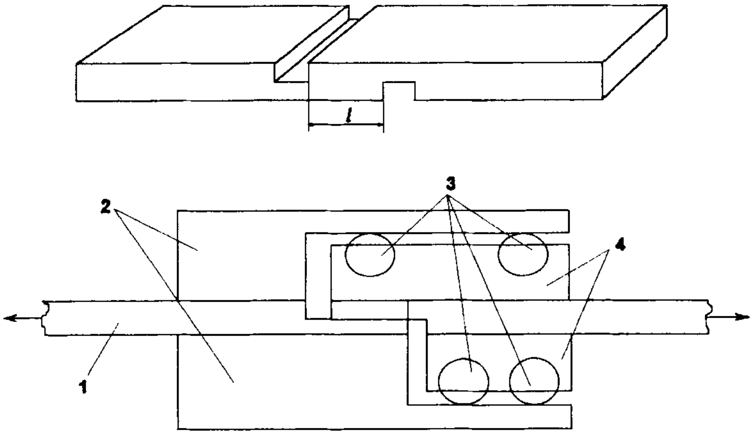

FIGURE 1 Specimen for determining the interlayer shear strength (a) and the diagram of the device for eliminating the effect of bending (b): 1 – specimen, 2 – holder, 3 – bearing, 4 – slide.

TABLE I Mechanical properties retention coefficients, measured at different temperatures after climatic ageing

Material grade	*Ageing time, years*	$k_R = R/R_0$*	
		$T = 293\ K$	$T = 353\ K$
Carbon Fiber Reinforced Plastics			
KMU-3, KMU-31, KMU-31n	3–9	0.92–1.11	1.15–1.31
KMU-4, KMU-41	5	0.97–1.13	1.05–1.36**
KMU-1, KMU-1u	10–11	0.62–1.08	0.34–0.72***
Organic Fiber Reinforced Plastics			
Organite 7T, 7TL, 10T	5–7	0.81–0.92	0.90–1.18
Organite 7TK	5	1.0–1.15	1.41–1.49
Organite 6TKS, 7TKS	7	0.55–0.65	0.50–0.60
Glass Fiber Reinforced Plastics			
VPS-5, VPS-7, FN, SK-5-211B, SSTF-N	2–7	0.55–0.90	0.42–0.85

* R = tensile strength, bending strength, tensile fatigue strength, Young modulus, shear modulus;
** $T = 423\,K$;
*** $T = 473\,K$.

[1, 3–5], that the surface of specimens is destroyed to a far greater degree than the inner layers. For instance, Table II shows the effect of the duration and conditions of ageing on the bending strength of the Organite 7T organic fiber reinforced plastic [5]. The increase in strength at the initial point of ageing is caused by the post-curing of the epoxy binder. As the example time increases, the strength of the composite is influenced, to an increasingly greater degree, by the processes of the destruction of the binder and the disorientation of the organic fiber.

A series of special purpose studies was carried out searching for indicators most sensitive to the ageing of the surface layers of PCM. Table III may serve as an illustration of these investigations. After 1 year of exposure in a warm humid climate, in this material, because of

TABLE II The bending strength (MPa) for Organite-7T organic fiber reinforced plastic after ageing in a warm humid climate

Ageing time, years	*Open-air specimens*	*Sheltered specimens*
0	524	524
0.5	586	605
1	577	606
2	529	584
4	475	550
6	429	496

TABLE III Organite 7TK parameters at $T = 353\,\mathrm{K}$ in the initial state and after 1 year of climatic ageing

Parameter, R	*In initial state, R_0*	*After 1 year of climatic ageing*	$K_R = R/R_0$
σ_t, MPa	301	391	1.3
σ_{-t}, MPa	87	84	0.97
G′, MPa	480	420	0.88
w_m, %	12.1	9.5	0.79
$D \cdot 100$, mm^2/days	2.02	5.06	2.50

the superposition of the effect of plasticization with water and post-curing of the binder, mechanical properties (tensile strength σ_t, bending strength σ_b, compression strength σ_{-t}, Young modulus E, dynamic shear modulus G' *etc.*) differ from the initial values no more than 30%.

Moisture diffusion coefficient D, determined by the moisture diffusion analysis (MDA) [4], changes in a totally different way. Due to the fact that this indicator is extremely sensitive to the state of specimen surface, its value grows 2.5 times after one year exposure of the composite.

Tensile fatigue strength σ_{-1} possesses a high sensitivity to the accumulation of defects on the surface of exposed PCM. We have arrived to this conclusion after fatigue tests of composites. For instance, for the organic SVM-fiber reinforced plastic with the binder of the BC-2526 K epoxypolysulfonate type, tensile strength and bending strength being unchanged, the value of tensile fatigue strength after a two year exposure in a climate, decreases by 16% (Fig. 2) [5]. However, this sensitive technique is characterized by a high labour-intensiveness and cost and, therefore, can hardly be used for the assessment of the surface damage in the aged PCM specimens.

Amount the mechanical indicators for the quantitative description of the inhomogeneity of climatic ageing across the thickness of PCM plates, is the interlayer shear strength τ_z. For the Organite 7T considered in Table II in the initial state and after six year of climatic ageing, results of measuring τ_z have also been obtained (Fig. 3). It turned out that the observed changes of the "effective" indicator σ_b are the result of a substantial gradient of parameter τ_z values in the aged specimens. In the central layer of plates $\tau_z = 18 \pm 2\,\mathrm{MPa}$, in the surface layers τ_z decreases to 10 – 13 MPA in the sheltered exposure

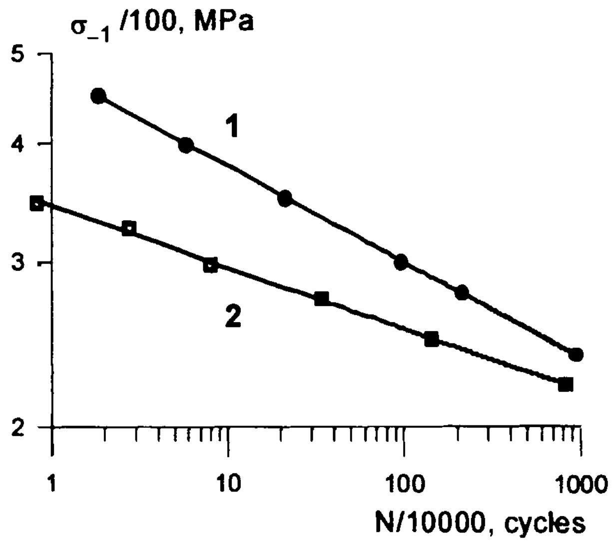

FIGURE 2 Fatigue curves of VS-2526K organic fiber reinforced plastic in the initial state (1) and after two years of climatic ageing (2).

and to 7–8 MPa in the open-air exposure. The discovered differences in the trend of the curves in Figure 3 can be explained by a distinct influences of climatic factors under direct solar radiation and under shelter. During the surface layer facing the Sun, which supports conclusions [3–5] regarding the active effect of solar radiation upon the ageing of organic fiber reinforced plastics under conditions of a warm humid climate.

As the second example, Figure 4 illustrates the strength gradient of interlayer shear of the glass fiber reinforced plastic of EDT-10 type 8 mm and 9 mm thick after 10 years of climatic ageing. It is evident from the figure that the value of τ_z is different for the inner and outer layers. Therefore, the gradient of properties across the thickness of a material is observed in the climatically aged specimens of PCM.

To find out the causes of such a change in parameter τ_z in the glass fiber reinforced plastic on the basis of EDT-10 binder, dynamic, mechanical and dilatometric studies have been carried out, which are described in paper [6]. The analysis of the result (Tab. IV) has revealed that the nature of change in the viscoelastic characteristics and the linear thermal expansion coefficient α does not coincide with the

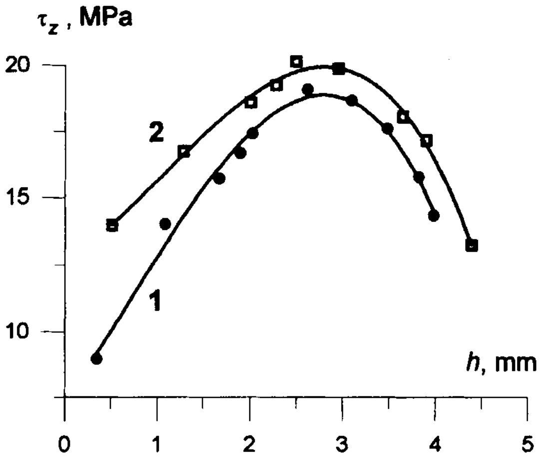

FIGURE 3 Change of strength during the interlayer shear across the thickness of the originate 7T plate after 6 years of ageing in the open air (1) and under shelter (2).

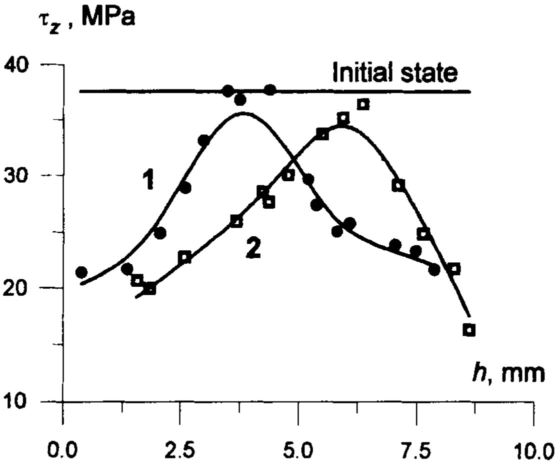

FIGURE 4 Effect of the strength gradient of interlayer shear after 10 years of climatic ageing of EDT-10 glass fiber reinforced plastic. Thickness: 1 – 8 mm, 2 – 9 mm.

changes τ_z across the thickness of the specimen. Indeed, the drop in G' measured at 293 K and in the glass transition temperature T_g from the center of the strength during the interlayer shear. That can be explained by the binder, whereas parmeter τ_z influences the state of the fiber-binder boundary.

TABLE IV Characteristics of individual layers of EDT-10 glass fiber reinforced plastic after 10 years of climatic ageing

	Glass transition temperature of a binder	*Dynamic shear modulus G', GPa*		*Linear thermal expansion coefficient $\alpha \cdot 10^6$, K^{-1}*	
	T_g, *K*	$T = 293\,K$	$T = 423\,K$	$T < T_g$	$T > T_g$
surface layer exposed to solar radiation	342	3.0	0.25	14.0	2.5
inner layer	333	5.0	0.28	11.8	4.9
surface layer without exposure to solar radiation	337	6.1	0.33	13.2	2.8

Using the data tabulated in Table IV that coincide with the characteristics of the glass fiber reinforced plastic VPS-7 [6], let us now attempt to explain the trend of the dependence $\tau_z(h)$ (Fig. 4). During ageing, it is primarily the outer layers of the material that are affected by a climate, therefore, the properties of the inner layers are the closest to the initial ones [6]. Two plates of the glass fiber reinforced plastic possess a difference in glass transition temperatures (with the plate thickness of 9 mm $T_g = 333$ K, at 8 mm -343 K). It has been proved [6] that during climatic ageing of VPS-7, post-curing of EDT-10 binder might be possible (the effect is observed in the surface layer exposed to solar radiation with the plate thickness of 9 mm).

A decrease in G' in the radiated layer of the glass fiber reinforced plastic confirms the presence of the binder description process. One can convince oneself that this is correct by a visual inspection: the irradiated side reveals the destruction and weathering of the binder, stripping of the filler. Thus, post-curing and destruction take place simultaneously in the epoxy binder of the glass fiber reinforced plastic in the course climatic ageing. Adhesive interaction on the binder-fiber interface is diminished.

Dilatometric measurements (Tab. IV) supported the regularity considered in [6]: during the transition of the binder from a glassy into a highly elastic state, the linear thermal expansion coefficient α is decreased. That might be possible due to the existence of internal tensions in the binder of the glass fiber reinforced plastic. Their presence in PCM contributes to the decrease in strength at the fiber-binder boundary during climatic ageing.

The analysis made for different PCM has demonstrated that the mechanical properties of those materials are determined during the process of climatic ageing both by the change in the interaction at the binder-fibrous filler boundary and the structural changes of the binder. To illustrate the point, a diffusion model of PCM on the basis of epoxy matrix was examined.

Mathematical experiment was also performed for the following model of the moisture diffusion in Alors (laminated pressed systems composed of thin aluminum alloys alternating with layers of organic fiber reinforced plastics):

$$\frac{\partial c}{\partial t} = D_{II}\frac{\partial^2 c}{\partial x^2} + D_{\perp}\frac{\partial^2 c}{\partial y^2} - B(x,y,t), \qquad (1)$$

where x-coordinate along aluminum sheet rolling; y-coordinate across aluminum sheet rolling; t-exposure time; c-relative moisture concentration; D_{II}-coefficient diffusion along rolling; $D_{\perp}$-coefficient diffusion across rolling; $B(x, y, t)$ is the function which responds for moisture penetration in Alors volume in the first approximation is different in defective edge and undamaged sample volume. The reason for the dependence of $B(x, y, t)$ on coordinates is the presence of defects in the edge after cutting of sample. Time dependence of $B(x, y, t)$ is explained by penetration of moisture into the interface polymer composite–aluminum and by the change in the sorption capacity due to the corrosivity of the aluminum alloy. It should also be noted that this change in the edge will be of a more intensive nature than in undamaged volume. The results of numerical experiment is presented on Figure 5.

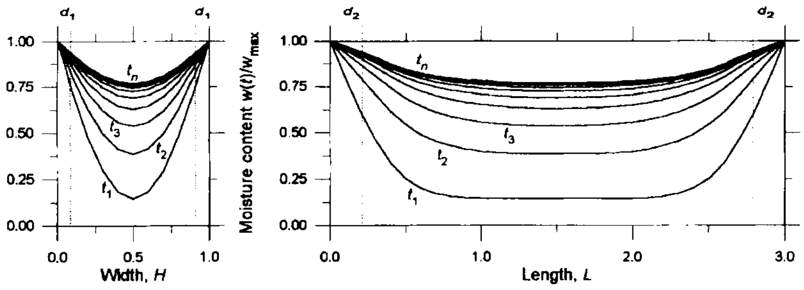

FIGURE 5 Numerical experiment of moisture penetration into Alor based on of (1); $t_1 < t_2 < t_3 < \cdots < t_n$-time moments.

This mathematical model (1) can describe the whole set of experiment data calculating five parameters only: w_{max} – saturated moisture content; D_{II} – coefficient diffusion along rolling; $D_{\perp}$ – coefficient diffusion across rolling; d_1 – edge size along rolling; d_2 – edge size across rolling.

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