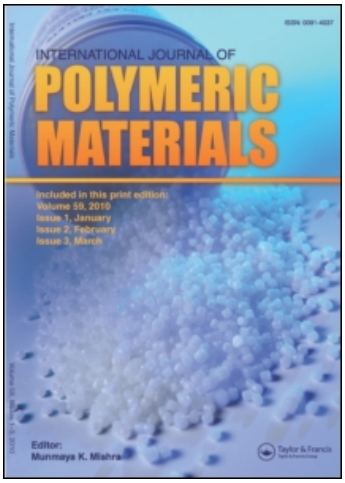


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# Climatic Ageing Of Organic Fiber Reinforced Plastics: Water Effect

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# Climatic Ageing Of Organic Fiber Reinforced Plastics: Water Effect

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Climatic stability of 14 organic fiber reinforced plastics for aerospace applications developed at the All-Russian Institute of Aviation Materials was studied. Plastics were exposed for 5–10 years under warm humid climatic conditions of the city of Batumi on the Black Sea Coast. It has been proven that observed changes in the strain-stress properties of organic fiber reinforced plastics result from the fact that moisture causes the following effects: reversible plasticization effect, change in structural heterogeneity of the epoxy binders, active postcuring of the epoxy binders, plasticization effect of the SVM-fiber.

*Keywords:* Plastics; composites; organic fibers; ageing; humidity properties

## INTRODUCTION

Organic fiber reinforced plastics (OFRP) is one of the most perspective classes of modern polymeric composite materials. In Russia, OFRP on the basis of the SVM-fiber (poly-*n*-amidobenzimidasol) and binders of an epoxy type are widely practised in aircraft-building. In aircraft-building, these materials successfully compete with glass fiber reinforced plastics, carbon fiber reinforced plastics, and aluminium alloys. However, when exploiting the aircrafts under real conditions, it is necessary to take into consideration the fact that OFRP properties may worsen, because of plasticizing effect of atmospheric humidity [1]. For this reason, when using materials of this class for airplanes and helicopters of all-climatic purpose, the information on peculiarities of OFRP ageing in a humid environment is needed.

In our previous papers [2–4], it is shown that OFRP features rather high climatic stability. However, for some grades of the materials, especially at high temperatures, significant change in initial parameters was observed. The purpose of this paper is to investigate the role of water at continuous climatic ageing of OFRP.

## EXPERIMENTAL

We performed the following experiment: OFRP were exposed for 5–10 years under warm humid climatic conditions of the City of Batumi on the Black Sea Coast. Plates or sheets of OFRP in the form of monolayer or pressed packs up to 1–6 mm thick were exposed in a free state and also under the impact of tensile and bending loads of operating level. Names of OFRP, epoxy binder variety, conditions of hardening, the tensile strength and bending strength in the initial state and after 3 years of exposure are listed in Table I.

Simultaneously, the same materials were tested in laboratory climatic chambers, in which we varied the temperature $T$and relative humidity $\varphi$ from 293 to 383 K and from 0 to 100%, respectively. Dynamic shear modulus $G'$, Young modulus $E$, bending strength $\sigma_b$, tensile strength $\sigma_t$, compressing strength $\sigma_{-t}$ were measured and moisture content was controlled in the materials at various stages of the exposure. To clear up the mechanisms of physical, chemical and structural transformations, the methods of dynamic mechanical analysis (DMA), linear dilatometry, optical and electron microscopy were used and moisture sorption and diffusion were studied. Detailed characteristics of these methods is provided in paper [1].

## RESULTS AND DISCUSSION

Table I shows that after only 3 years of exposure in a warm humid climate, an OFRP strength, on the average, goes down 12–15%, and for some brands of materials $\sigma_t$ and $\sigma_b$ reduction is up to 30%. The samples exposed, as shown in Table II, contain 3.5–4% of water. After drying the aged OFRP at 353 K, $\sigma_t$ change is insignificant, while $\sigma_b$ goes up 10–15%.

TABLE I Comparison of OFRP stability in initial state and after 3 years of climatic ageing

| *OFRP name* | *Epoxy binder, conditions of hardening* | *Initial state* | | *After 3 years of exposure* | |
|---|---|---|---|---|---|
| | | *tensile stength* $\sigma_{t0}$, MPa | *bending strength* $\sigma_{b0}$, MPa | $\sigma_t/\sigma_{t0}$ | $\sigma_b/\sigma_{b0}$ |
| Organite 5T | EP-2MK | 720 | 415 | 0.91 | 0.82 |
| Organite 7T1[a] | 5-211B | 678 | 402 | 0.74 | 0.70 |
| Organite 7T2 | 5-211B $T=423$K, $p=0.5$ MPa | 731 | 441 | 0.94 | 1.07 |
| Organite 7TK | 5-211B $T=398$K, $p=0.5$ MPa | 523 | 416 | 1.07 | 0.76 |
| Organite 7TL | 5-211B $T=423$K, $p=10$ MPa | 820 | 441 | 0.91 | 0.93 |
| Organite 7TLR[b] | 5-211B $T=423$K, $p=10$ MPa | 850 | 563 | 1.01[d] | 0.99[d] |
| Organite 10T | UP 2227 | 740 | 470 | 0.84 | 0.90 |
| Organite 11T | VK-36R | 620 | 470 | 0.75 | 0.76 |
| Organite 12T | EDT-69N | 659 | 343 | 0.93[d] | 0.89[d] |
| Organite 16T | VS-2526K | 647 | 515 | 0.92[d] | 0.88[d] |
| Organite 6TKS[c] | EDT-10 | 809 | 453 | 0.75 | 0.88 |
| Organite 7TKS[c] | 5-211B | 878 | 469 | 0.68 | 0.80 |
| Organite 12TKS-42-2[c] | EDT-69N $p=2$MPa | 765 | 553 | 0.91 | 0.79 |
| Organite 12TKS-42-5[c] | EDT-69N $p=5$MPa | 787 | 570 | 0.93 | 0.83 |

a- material of SVM fiber made in 1974 with low stability was used
b- material of SVM fiber with prior radiation treatment was used
c- material of SVM fiber and VMP fiber glass in 2:1 ratio was used
d- after 2 years of exposure

TABLE II Tensile strength and bending strength retention coefficients for OFRP after ageing in a warm humid climate

| *Material name* | *Ageing time, years* | *Moisture content, %* | *Retention coefficient* $K_R=R/R_0$ *without drying* | | *after drying* | |
|---|---|---|---|---|---|---|
| | | | $K_{\sigma t}$ | $K_{\sigma b}$ | $K_{\sigma t}$ | $K_{\sigma b}$ |
| Organite 5T | 3 | 4.0 | 0.91 | 0.82 | 0.93 | 0.95 |
| Organite 7T2 | 8 | 4.0 | 0.86 | 0.90 | 0.87 | 0.92 |
| Organite 10T | 8 | 4.3 | 0.85 | 0.87 | 0.92 | 0.96 |
| Organite 11T | 4 | 3.5 | 0.73 | 0.70 | 0.79 | 0.85 |
| Organite 12T | 2 | 3.8 | 0.93 | 0.89 | 0.93 | 0.89 |
| Organite 6TKS | 7 | 3.6 | 0.44 | 0.42 | 0.49 | 0.62 |
| Organite 7TKS | 7 | 3.6 | 0.45 | 0.37 | 0.54 | 0.62 |

drying temperature is $353 \pm 10$ K

When measuring the tensile strength, the main load is taken up by the SVM fibers, and when measuring the bending strength, significant part of the load is taken up by the binder. Hence it follows that during a continuous exposure under the climatic conditions, SVM fiber undergoes irreversible changes, while in epoxy binders, the changes are partly reversible, because of the plasticizing moisture.

OFRP exposure to saturation at $T = 353$ K and $\varphi$ 100% in a climatic chamber significantly increases the effects described above (Table III) In this case, the quantity of the sorbed moisture goes up to 5–15%. Mechanical properties retention coefficients for moisture saturated OFRP are, on the average, 0.75, while, after additional drying, they go up to 1.05. Thus, the properties of some OFRP improve after exposure in a humid environment at high temperatures.

In order to better understand the character of water interaction with the OFRP components, we have performed cyclic thermal and moisture tests of Organite 7 T1 under the conditions of moistening followed by drying. For this purpose, sample of Organite 7 T1 of three geometrical shapes (65 × 60, 120 × 10 and 120 × 4, all 2.25 mm thick) were exposed at $T = 353$ K and $\varphi = 100\%$ for 1,000 hours, and then dried at the same temperature during the same period of time. Overall, we have performed 8 cycles with overall duration of about 2 years.

Figure 1 compares the kinetics of Organite 7 T1 tensile strength in the first cycle of moistening and at the exposure in a warm humid climate.



TABLE III Change of mechanical properties retention coefficients for moisture-saturated OFRP accounting for drying

| *Material grade* | *Moisture sorption at* $353 \pm 3K$, $^{o}_{o}$ | *Mechanical properties parameter, R* | *Retention coefficient* $K_R = R/R_0$ | |
|---|---|---|---|---|
| | | | *without drying* | *after drying* |
| Organite 5T | 16.8 | G′ | 0.67 | 0.89 |
| Organite 7T2 | 8.9 | G′ | 0.75 | 0.94 |
| | | $\sigma_b$ | 0.62 | 0.80 |
| | | $\sigma_c$ | 0.68 | 0.92 |
| Organite 10T | 15.1 | G′ | 0.64 | 1.16 |
| Organite 12T | 6.9 | G′ | 0.83 | 1.22 |
| | | $\sigma_c$ | 0.85 | 1.20 |
| Organite 16T | 5.3 | $\sigma_b$ | 0.80 | 1.10 |
| | | $\sigma_c$ | 0.71 | 1.25 |

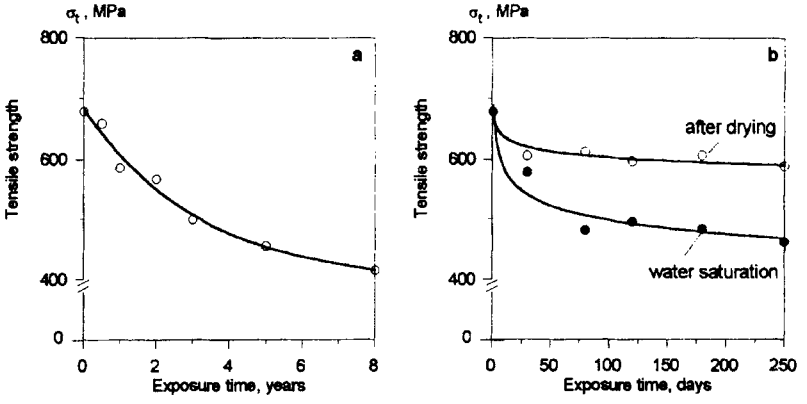



FIGURE 1 Change of tensile strength of Organite 7T1 after exposure in a warm humid climate (a) and in a climatic chamber at $\varphi = 100\%$, $T = 333$ K (b).

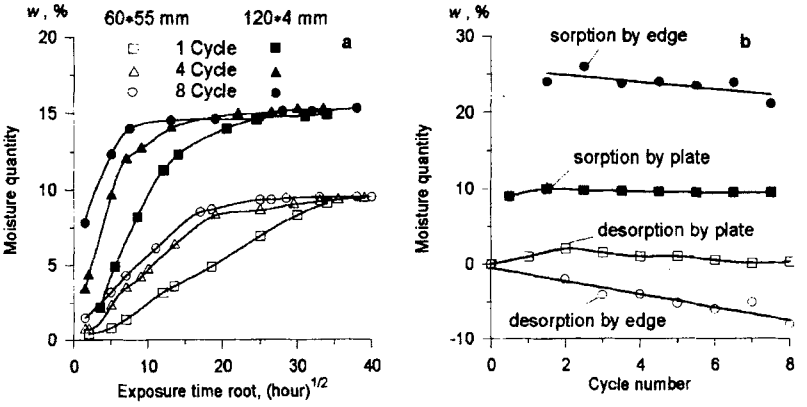



FIGURE 2 Isotherms of moisture sorption of Organite 7T1 samples of two shapes in different cycles (a) and the value of maximum moisture content in the edge area and in the undamaged part of the plate in the phases of sorption and desorption (b).

The maximum reduction in $\sigma_t$ of this material in a wet condition is 30%, and after drying the water saturated samples, it is only 15%.

The isotherms of moisture sorption for Organite 7T1 of two shapes for different cycles are shown in Figure 2a. The difference in the value of the maximum moisture-saturation $w_\infty$ is caused by the influence of the defect edge occuring during the cutting of OFRP plates. The results of

the sorption and desorption changes follow the ratio.

$$w_{\chi} = w_{1\chi} V + w_{2\chi}(1 - V) \tag{1}$$

where $w_{1\chi}$ and $w_{2\chi}$ is the maximum moisture concentration in the edge area and in the undamaged part of OFRP, $V$ is the volume part of the edge. According to the computer-processed data, the edge thickness is 0.7 mm. Figure 2b shows that, at the increase in the number of cycles, the moisture content of the undamaged part of OFRP undergoes only very little change and is about 10%. In the edge area, this value is 24%, and during the cyclic process, the binder mass in the edge area decreases linearly in the desorption stage.

The effects of moisture interaction with OFRP were researched using the DMA method [1]. In the samples of Organite 7T1 in the initial state and after each semi-cycle, we used torsion pendulum to measure dynamic shear modulus $G'$ and mechanical loss tangent tg$\delta$ in the temperature range 293–573 K. Figure 3 shows the temperature dependencies tg$\delta$ and $G'$ of Organite 7T1 and its components: SVM monofiber and separately hardened 5-211B binder. DMA method provides information on the nature of glass transition of epoxy binder ($\alpha$-peak of tg$\delta$ at 383 ± 3K) and SVM fiber ($\alpha$-peak of tg$\delta$ at 540 ± 3K). The height of these maxima in OFRP is measured by the law of mixture. Glass transition

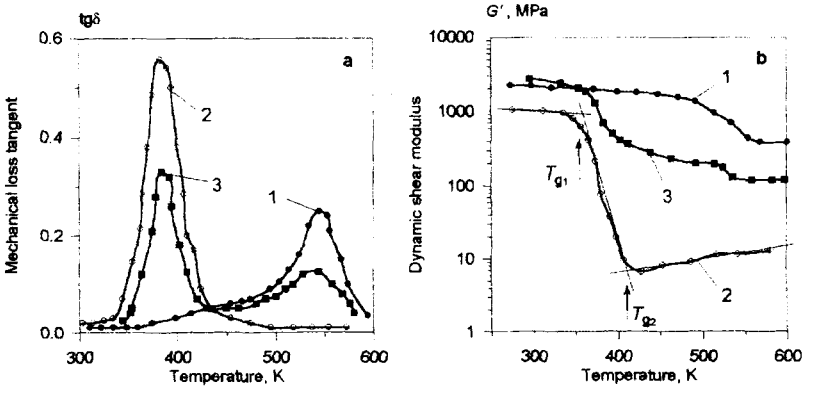



FIGURE 3 Temperature dependencies $tg\delta$ (a) and $G'$ (b) of SVM monofiber (1), separately hardened 5–211B binder (2) and Organite 7T1 (3).

temperatures ($T_{g1}$ is the beginning and $T_{g2}$ is the end) are defined by the crossing of straight lines defining the incidence of $G'(T)$ curves in the area of α-transition (Fig.2b).

For comparison, Figure 4 shows $G'(T)$ and $tg\delta(T)$ dependencies of Organite 7T1 in the initial state and in the stages of moistening and drying in Cycle 8. This figure explicitly reflects the effects of moisture influence on both the binder and the SVM fiber. At water saturation, $G'$ of OFRP goes down 35% in a glassy state which is the indication of plasticizing, $G'$ dependence on the number of cycles is shown in Figure 5. However, for the given material, as well as for other OFRP names (Tables 2,3), plasticizing by moisture is not a completely reversible effect: after drying, the value $G'$ is less than the initial one.

For the epoxy binders, water is a typical polar plasticizer. However, on moisture sorption, some effects are often observed, differing not only quantitatively, but also qualitatively from known plasticization regularities. In the majority of epoxy binder $T_g$ is regularly decreased on moisture saturation [1], but in this case it is increased (Fig. 4.5), which is inconsistent with plasticization ideas.

The decrease in $T_g$ with increasing moisture content is known to be described by the equation

$$\frac{dT_g}{dw} = -k(T_g - T_{g\infty}) \tag{2}$$

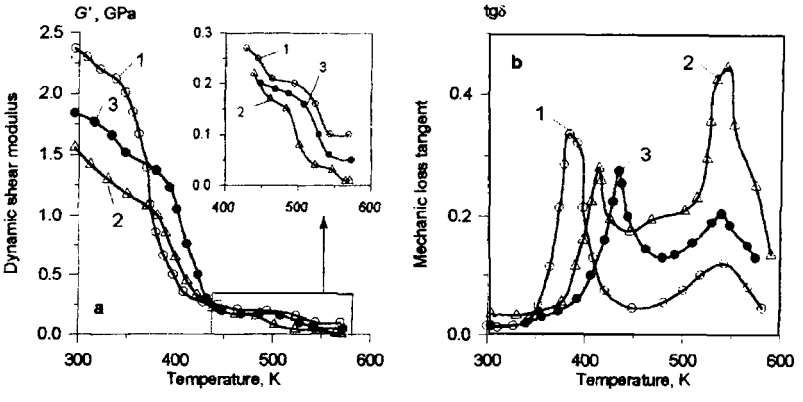



FIGURE 4 Temperature dependencies $G'$ (a) and $tg\delta$ (b) of Organite 7T1 in the initial state (1), after moistening in Cycle 8 (2) and after drying in Cycle 8 (3).

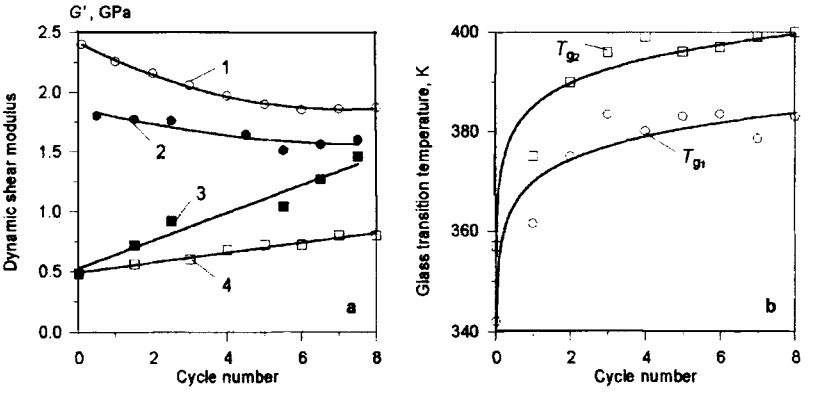



FIGURE 5 Influence of the number of cycles on: a) DMA-indicators of Organite 7T: G' at $T = 293$ K (1,2) and $tg\delta$ in the area of $\alpha'$-relaxation at $T = 540$ K (3,4); (1,4) — after drying; (2,3) — after moistening; b) glass transition temperatures of dried samples, corresponding to the beginning ($T_{g1}$) and end ($T_{g2}$) of $\alpha$-transition in 5-211B binder.

with a limiting condition $T_g = T_{go}$ at $w = 0$; $T_g = T_{g\infty}$ and $dT_g/dw = 0$ at $w_\infty$, where $w_\infty$, is the maximum quantity of moisture. Hence, the ratio

$$\ln(T_g - T_{g\infty}) = -kw + \ln(T_{g0} - T_{g\infty}) \tag{3}$$

allows a predicted decrease, $T_g$ i.e. plasticizing effect of moisture in epoxy binders.

However, the ratio (3) is true only for the case, when water is sorbed by polymer in a glassy state. It applicability is limited by the glass transition temperature $T_{g1}$. According to paper [5], the structural heterogeneity increases in epoxy matrices in a process of moisture saturation at $T > T_{g1}$. Its essence is in the fact that water molecules weaken molecular interactions in the epoxy binders and, due to segmental mobility, provide closer packing and perfection of the amorphous phase. Macroscopic manifestation of this effect is an increase in the density, mechanical parameters, reduction of linear thermal expansion coefficient, and also increase in $T_g$ [5,6].

This effect is not the only reason for deviation of the experimental values of $T_g$ from the theoretical ones, calculated by the formula (3). Water was found to activate postcure of the epoxy materials for a whole class of epoxy compounds, used in OFRP [6]. In the 5-211B binder, with

unreacted reactive groups segmental mobility is facilitated and the probability of contact of functional groups is increased due to plasticizing effects. This effect contributes to the formation of additional chemical bonds and, as a consequence, $T_g$ increases.

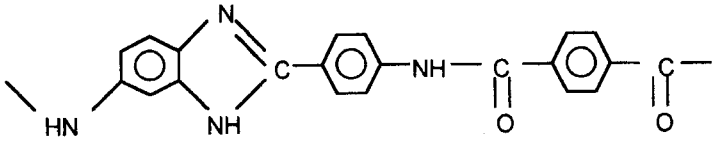
Thus, the final result of mosture absorption (Fig. 4,5) is determined by a competition between the effects of plasticization leading to a decrease in $T_g$ and postcure leading to an increase in $T_g$. In this case the $T_g$ dependence with change in $w$ is governed by ratio [1]

$$T_g = T_{gw_i} \exp[(k_2 - k_1)(w - w_i)], \tag{4}$$

where $i = 0,1,2$ are respectively the three regions of moisture concentration in the epoxy binder ($0 < w < w_1$, $w_1 < w < w_2$, $w > w_2$), $w_1$ is the concentration at which postcure is initiated, $w_2 = w_\infty$ is the compatibility limit above which the water is precipitated as a separate phase. The coeffients $k_1, k_2$ and $T_{gw_i}$ can be determined from the limiting conditions.

The role of water in the interaction with SVM-fibre is important. In our case, the plasticizing effect is expressed by the significant, partly reversible, increase in the height of $\alpha$-peak of tg$\delta$ for the Organite 7T1 cycled samples (Fig. 4b, 5a). The investigation of X-ray diffraction shows [7], that SVM plasticizing by moisture is accompanied by disorientation of the fiber.

The repeated chain of SVM




consists of diamine and dianhydride components. In the initial oriented state, SVM fiber has mostly trans-conformers fixed by H-links. Moistening makes it possible to make a transition from trans- to cis-shape which is partly reversible. This conformation-isomeric regrouping in SVM fiber is the cause of irreversible reduction in stability and elasticity module of OFRP [7,8]. Figure 4, 5 provide quantitative information on the contribution of SVM fiber to reversible and irreversible changes in

mechanical properties of Organite 7T1 in the process of thermal and moisture cycling.

## CONCLUSION

The changes observed in the strain-stress properties of OFRP result from the fact that absorbed moisture causes the following effects:

- Reversible plasticization effect under which the glass transition temperature of a binder drops, the strength and hardness of OFRP are reduced at $T < T_g$;
- Change in structural heterogeneity of epoxy and thermoplastic binders, depending on the concentration and the nature of water molecular condensation in polymer;
- Active postcuring of epoxy binders. Essentially, the effect is as follows. After pressing of a pack, finished OFRP contains unreacted reactive groups. On moisture sorption, segmental mobility becomes easier and the probability of contact between functional groups increases in a binder because of plasticization effect;
- Plasticization effect, change in a liquid-crystalline structure and disorientation of SVM fiber, which involves an irreversible reduction in strength and hardness of reinforced element of OFRP.

The results obtained from the investigation provide a basis for the development of molecular models of OFRP ageing in a humid environment and for the prediction of operating capacity of this type composite materials under true operating conditions.



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