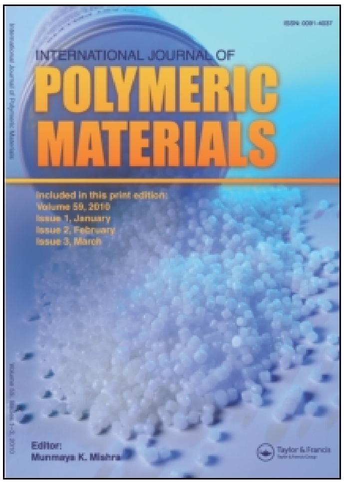

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Effect of Climatic and Radiation Ageing on Properties of Glass Fiber Reinforced Plastic VPS-7

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The effect of radiation on the properties of glass fiber reinforced plastic of VPS-7 type on the basis of EDT-10 epoxy binder was investigated. Radiation treatment with the maximum dose of 30 MGy was performed for glass fiber reinforced plastic samples in the initial state and after 0.5, 1, 2, and 5 years of exposure in the zones of cold, moderate and warm damp climate. Evaluation of climatic and radiation resistance was conducted by the change in bending strength, interlayer shear strength, Young modulus. Methods of dynamic mechanical analysis and linear dilatometry were employed to investigate the state of epoxy binder during ageing. It has been established that radiation treatment of both initial and climatically aged VPS-7 samples, causes the destruction of the boundary (epoxy binder – glass fiber). The discovered extreme increase of mechanical characteristics of glass fiber reinforced plastic is explained by the competing effects of these two processes. In this case, there is a lack of indications to the occurrence of additional joinings of epoxy binder molecules during irradiation. It has been proved that ageing conducted according to the reverse scheme (radiation treatment with subsequent exposure in the climate) is more rigid and intensifies the effects of the change in the properties of the glass fiber reinforced plastic.

Keywords: Glass fiber reinforced plastic; climatic ageing; γ-irradiation; destruction; bending strength; interlayer shear strength; Young modulus; glass transition temperature

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INTRODUCTION

Modern polymeric composite materials have excellent mechanical properties in the initial state. However, when operating aircraft and spacecraft, ageing processes are progressing in polymeric materials [1]. These ageing processes can significantly deteriorate the complex of stress–strain properties of the materials and can make individual components of the product fully unusable.

Experimental results, concerning the environmental and γ-irradiation effects on the mechanical properties of the glass fiber reinforced plastic are presented in this paper.

EXPERIMENTAL

The effect of γ-irradiation upon the properties of VPS-7, pre-exposed in various climatic zones, has been studied. To carry out tests, glass fiber reinforced plastic plates (binder marks EDT-10P, 29%, filler–glass cloth of T-10 mark) of 300 × 300 × 5 mm sizes, were used. Exposure was performed in the course of 5 years, in conditions of warm, humid (Batumi), moderate (Zvenigorod) and moderately cold (Murmansk) climates. Exposure duration of τ constituted 0.5, 1, 2 and 5 years.

After conditioning in laboratories, unexposed and exposed VPS-7 samples were subjected to γ-irradiation. Radiation treatment was performed in the air by γ-radiation ^{60}Co with radiating power of 55 ± 10 Gy/sec. Maximum dose of radiation constituted $3 \cdot 10^7$ Gy.

For a certain part of samples the sequence of exposure was changed: the radiation treatment preceded the exposure in a climate. That allowed to verify the equivalency of exposure by the $\tau + \gamma$ and $\gamma + \tau$ schemes (where τ – exposure in climate, γ-irradiation).

Evaluation of climatic and radiation resistance was performed by changing bending strength σ_b, interlayer shear strength τ_z, Young modulus E. Preliminary check showed that the spread in initial values of stress–strain characteristics from plate to plate, is substantial and can reach 30%. Therefore, at each regular stoppage of tests after climatic ageing, a separate plate was provided, from which samples were made for radiation treatment and for determining mechanical indicators. More stable indicators turned out to be: dynamic shear modulus G', mechanical loss tangent tgδ, linear thermal expansion coefficient α_T and glass transition temperature T_g. For that reason, the main studies were performed by the dynamic mechanical analysis and the linear dilatometry methods in the temperature interval of 293–450 K.

RESULTS AND DISCUSSION

A substantial spread in values of σ_b and E of the glass fiber reinforced plastic from plate to plate hampered the evaluation of the climatic ageing effect upon the mechanical properties. It has been established, that values of σ_b after various periods of ageing in three climatic zones, fluctuate near the mean value of 250 ± 60 MPa and do not differ from their initial value. In a similar way, Young modulus is retained as well (9.8 ● 1.5 GPa). Consequently, the change in the mechanical indicators were normalized to the corresponding characteristics of unradiated samples for each individual plate (Tab. I). The table shows that with the increase of radiation dose up to 30 MGy, the mechanical characteristics of VPS-7 increase by 10–15%. In climatically aged samples, as the radiation does increases to 5–15 MGy, σ_b and E also increase by 30–50% and then after 30 MGy, somewhat go down.

To ascertain molecular processes taking place during climatic and radiation ageing, measurements of dynamic shear modulus G', mechanical loss tangent tgδ and sound velocity c_t, were performed in the temperature interval of 293–450 K. VPS-7 samples were used, cut out from the surface layer of plates 0.8 mm thick. Temperature dependencies of the measured values in the initial state, are given in Figure 1.

These dependencies are typical for the epoxy compounds [1, 2] and can be used to obtain information about the behavior of the binder in the α-relaxation area, *i.e.*, in the glass transition region. Decrease of G' from 4.9 GPa at 293 K to 1.2 GPa at 433 K, determines the initial effect of the decrease in the rigidity of VPS-7 at the expense of softening of EDT-10P binder at α-relaxation. Curve tg$\delta(T)$ shows the softening of the binder in the shape of a double peak, the apexes of which determine the heat stability of the matrix (at 390 and 373 K), in its more densely packed, ordered sections and in porous disordered regions. These two levels of the epoxy binder structure correspond to

TABLE I Bending strength and Young modulus retention coefficients for VPS-7 after climatic and radiation ageing

Radiation dose, MGy	*Duration of exposure in a climate (years)*	$K_\sigma = \sigma/\sigma_0$ *After exposure in climate*			$K_E = E/E_0$ *After exposure in climate*		
		cold	*moderate*	*humid*	*cold*	*moderate*	*humid*
1	0	1	1	1	1.09	1.09	1.09
	0.5	1.12	1.18	1.06	1.06	1.07	0.98
	1	1.13	1.21	1.25	1.06	1.03	1.01
	2	1.27	1.19	1.18	1.5	1.19	1.05
	5	1.14	1.11	1.18	1.07	1.11	1.07
2.5	0	1.1	1.1	1.1	0.95	0.95	0.95
	0.5	1.15	1.13	1.03	1.03	1.23	1.01
	1	1.15	1.26	1.3	1.08	1.1	1.05
	2	1.4	1.3	1.3	1.61	1.22	1
	5	1.19	1.25	1.38	1.01	1.09	1.11
5	0	1.17	1.17	1.17	0.97	0.97	0.97
	0.5	1.19	1.18	1.1	1.08	1.31	1.06
	1	1.23	1.26	1.45	1.12	1.05	1.2
	2	1.47	1.3	1.35	1.71	1.26	0.94
	5	1.23	1.35	1.5	0.99	1.09	1.12
15	0	1.07	1.07	1.07	1.01	1.01	1.01
	0.5	1.27	1.23	1.07	1.06	1.3	1.01
	1	1.28	1.31	1.4	1.21	1.16	1
	2	1.6	1.38	1.5	0.83	1.14	1.01
	5	1.23	1.25	1.45	1.04	1.07	1.12
30	0	1.07	1.07	1.07	1.14	1.14	1.14
	0.5	1.23	1.15	1.1	0.98	1.16	1.02
	1	1.18	1.31	1.4	1.15	1.07	1.09
	2	1.45	1.3	1.3	0.68	1.38	0.75
	5	1.16	1.16	1.25	1.04	1.01	0.99

the 4 characteristic temperatures $T_1 - T_4$ determined by the breaks of the curve on the chart $c_t(T)$.

Temperatures T_1 and T_3 are the beginning and the end of the α-transition in the disordered matrix of the EDT-10P binder, and T_2 and T_4 show the boundaries of the same transition in the ordered phase [2]. Generally, T_2 is taken as the glass transition temperature (T_g).

The results of measuring the dynamic mechanical characteristics of VPS-7 samples aged in the toughest climatic conditions (Batumi) with subsequent radiation treatment are presented in Table II and illustrated by the curves tg$\delta(T)$ in Figure 2 during the ageing in various climatic zones.

Analysis of data obtained has shown that the climatic ageing has practically no effect on the value G' of the material in the glassy state of its binder (T_g = 293 K), but to larger degree, it affects the change of

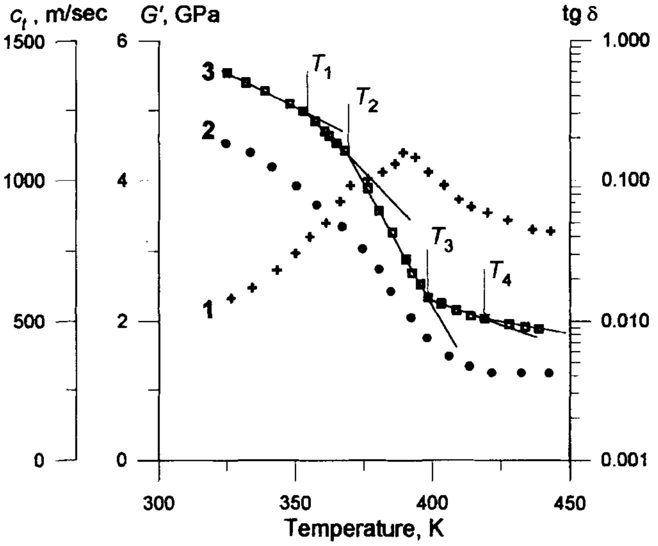

FIGURE 1 DMA-curves of glass fiber reinforced plastic VPS-7 in the initial state: 1 – tgδ; 2 – G'; 3–c_t.

TABLE II Effect of climatically and radiation ageing on dynamic shear modulus and characteristic temperatures in glass transition region of matrix of VPS-7

Duration of ageing, years region K	*Radiation dose, MGy*	*G', GPa at temperatures, K* 293	433	*Characteristic temperature of α-transition K* T_1	T_2	T_3	T_4	*Maximum temperature of tgδ dependence in α-transition*
0	0	4.9	1.2	353	368	399	420	390
	5	5	0.9	323	348	372	393	372
	15	4.8	0.6	311	328	363	379	356
	30	4.5	0.3	309	311	343	368	338
0.5	0	5	1.4	351	375	403	417	401
	5	5.2	0.9	323	353	373	393	366
	15	5.5	0.4	313	325	353	371	353
	30	5.8	0.3	311	318	348	363	343
2	0	4.9	1.3	341	375	401	417	401
	5	4.9	0.8	313	343	366	380	368
	15	5.5	0.6	317	329	367	383	357
	30	6	0.4	310	325	355	375	355
5	0	4.8	0.9	310	341	397	397	373
	5	4.7	0.4	319	331	363	387	357
	30	4.5	0.3	305	315	343	370	340

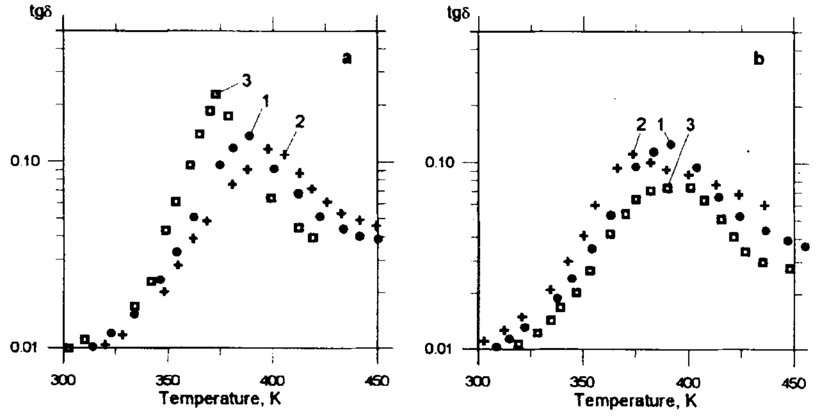

FIGURE 2 Temperature dependencies of tgδ at climatic ageing of glass fiber reinforced plastic VPS-7 in conditions of warm humid (a) and moderate climate (b) in initial state (1) and after exposure during 2 (2) and 5 years (3).

this characteristic in a highly elastic state of the binder. As the ageing period in a moderate climate (Zvenigorod) increases, the maximum temperature on dependencies tgδ and G' in a highly elastic increases monotonously. In a similar way, these parameters also change at the initial stage of ageing (the first two years) in a humid climate (Batumi) as a whole, the climatic ageing causes profound changes in the properties on the surface layer of the fabric based laminate.

Investigation of the effect of γ-radiation on the behavior of tgδ in the region of VPS-7 α-relaxation in the initial and aged state in Batumi conditions (5 years), has shown that with the increase in the radiation dose, characteristic temperatures of α-transition and values of G' decrease substantially in the highly elastic state (Fig. 3).

To verify the validity of conditions regarding the mechanism of the radiation ageing of the VPS-7 glass-cloth-base laminate, dilatometric studies of this material have been performed. Dilatograms obtained are given in Figure 4, whereas the values of temperature coefficients of linear expansion α_T, depending on the radiation dose, are presented in Table III.

For initial samples, VPS-7 on the initial section of the dilatometric curve (Fig. 4, curve 1), α_T constitutes $7{\cdot}10^{-5}\,K^{-1}$ and after excess of the glass transition temperature, it decreases to $7{\cdot}10^{-5}\,K^{-1}$. Similar regularity is typical for all samples. As a result of climatic ageing,

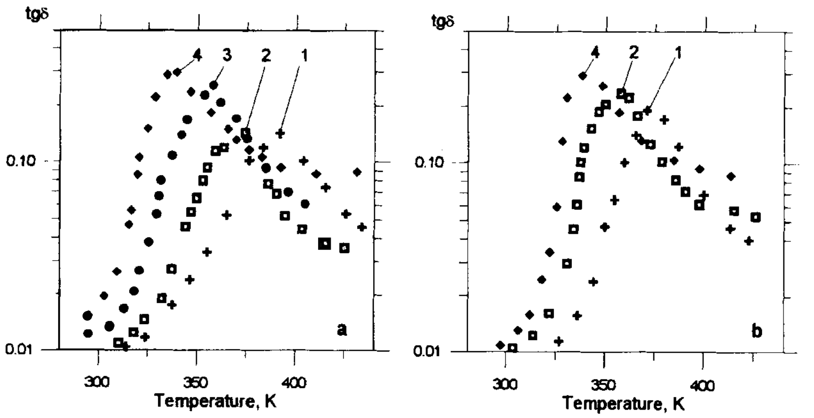

FIGURE 3 Temperature dependencies of tgδ at climatic of glass fiber reinforced plastic VPS-7 in initial state (a) and after exposure during 5 years; (b) in conditions of warm humid climate at radiation dose 0 (1), 5 (2), 15 (3) and 30 MGy (4).

TABLE III Linear thermal expansion coefficient of glass fiber reinforced plastic VPS-7 after climatic and radiation ageing

Duration of ageing (years)	*Radiation dose (MGy)*	$\alpha_T \cdot 10^5\ K^{-1}$, *in climatic conditions:* *warm, humid climate* $T < T_g$	$T > T_g$	*moderate climate* $T < T_g$	$T > T_g$
0	0	7	2	–	
	5	9.8	2.2	–	–
	15	9.7	2.2	–	–
	30	9.5	1.8	–	–
0.5	0	7.1	2.1	7.1	2.1
	5	10	2.3	8.7	1.8
	15	9.6	2.3	–	–
	30	8	1.5	–	–
1	0	8.9	2.3	8.2	2.4
	5	9.5	1.5	–	–
	15	9	1.6	–	–
	30	9	1.6	–	–
5	0	14.2	2.6	9	2.5
	5	14.8	2	–	–
	30	10	1.5	–	–

values of α_T at $T < T_g$ increase, the effect being more pronounced for the composite material aged in conditions of a humid climate. At $T > T_g$, as the ageing time increases, the increase of α_T is insignificant.

Decrease in values of α of VPs-7 at $T > T_g$ shows that during the softening of the binder, a significant role is played by the shrinkage

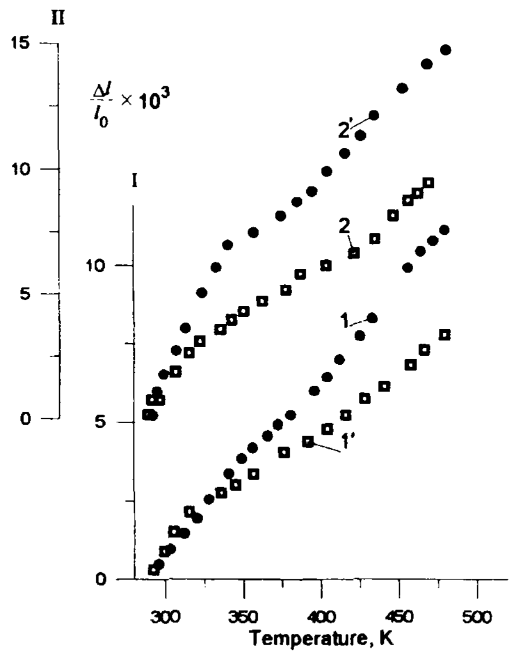

FIGURE 4 Dilatograms of VPS-7 samples in initial state (1, 1') and after 5 years of climatic ageing in a warm humid climate (2, 2') without radiation treatment (1, 2) and after influence of radiation dose 30 MGy (1', 2'). Numbers of axes respond to numbers of curves.

effect due to the presence of internal stress. One can draw a conclusion that as the ageing duration increases the internal stress remains or can be slightly decreased because the value of α at $T > T_g$ after 5 years increases from $2 \cdot 10^{-5} K^{-1}$ to $2.6 \cdot 10^{-5} K^{-1}$.

The aforesaid results also allow us to reveal the mechanism of physical and chemical transformations in EDT-10P binder during the climatic ageing. Much as other polymer composite materials, the properties of the glass-cloth-base laminate in question are determined by the superposition of two processes: post-curing and the destruction of the binder [2, 3]. At the initial stage of ageing, the dominant role is played by the post-curing process, the indicators of which are: rise in temperature of α-transition, characteristic temperatures $T_1 - T_4$ and values of G' in the highly elastic state (Fig. 1, Tab. II). As the time of ageing increases up to 5 years, the destruction process predominates in the surface layer of the glass-cloth-base laminate, which is proved by the lowering of temperatures $T_1 - T_4$ and G' at $T > T_g$.

Obviously, it was of interest to answer the following question: is the ageing according to scheme $\tau + \gamma$ (natural ageing plus radiation treatment) identical to the one according to the reverse scheme $(\gamma + \tau)$? To answer the above question, measurements of dynamic mechanical characteristics and α were performed and the results are given in Table IV.

As is obvious from Table IV, the nature of change in relaxation properties of VPS-7 both in scheme $\tau + \gamma$ and $\gamma + \tau$, fits into the framework of the studied regularities. However, ageing according to $\gamma + \tau$, for the composite material in question is more rigid than according to the reverse scheme $\tau + \gamma$. This is, probably due to the fact that the destruction of the binder during the γ-radiation treatment of VPS-7 samples takes place through the whole depth of the fabric-based laminate with practically the same intensity, whereas the destruction during the climatic ageing starts from the surface of the material.

Thus, the effects of $\gamma + \tau$ and $\tau + \gamma$ on VPS-7 are nonequivalent; in terms of the degree of destruction, the former regime is more aggressive.

The dependence of any of the parameters given in Table I on the time of the climatic ageing of τ, can be described by the kinetic equation [4].

$$y_i = A_{i1}e^{-k_{i1}\tau} - A_{i2}e^{-k_{i2}\tau} + y_{i\infty}, \tag{1}$$

where k_{i1} and k_{i2} are the constants of the rate of destruction and jointing respectively; A_{i1} and A_{i2} are pre-exponential factors; $y_{i\infty}$ is the limiting values of y_i at $\tau \to \infty$. From Eq. 1) it follows, in particular, that function y_i has a maximum at $k_{i2} > k_{i1}$, provided the jointing rate constant exceeds the destruction constant.

TABLE IV Interlayer shear strength for VPS-7 exposed in a moderate climate after various doses of irradiation

Dose of γ-radiation (MGy)	*Interlayer shear strength (MPa)*
0	7.8
5	8.3
15	8.5
30	9.1

The change in characteristic temperatures of the α-transition depending on the dose of γ-radiation approximates satisfactorily with the relationship:

$$\Delta T = \Delta T_{\infty}(1 - e^{-kD}), \tag{2}$$

where $\Delta T_{\infty} = T_{\infty} - T_0$; T_0 and T_{∞} – characteristic temperatures of the sample without radiation and after dose $D \rightarrow \infty$; k-radiation destruction coefficient. By way of illustration, Table V shows the values of parameters ΔT_{∞}, T_{∞}, T_0 and k for the maximum temperature of α-transition for VPS-7.

The extreme increase in values of σ_b and E as the radiation dose D is increased in Table I, is generally attributed to the occurrence of additional joints between the molecules of epoxy binder due to radiation effect. However, such a view is at variance with the decrease in temperature T_g and other characteristic temperatures of α-transition as the radiation dose increases for all investigated samples. Another important indication – the decrease of G' at $T > T_g$ depending on the dose of radiation both in initial and climatically aged samples – proves that radiation causes the destruction of the binder.

To explain the extreme increase of σ_b and E in glass fiber reinforced plastic with the increase of the radiation dose up to 5 – 15 MGy (Tab. I), it might be presumed that along with the destruction during γ-radiation, the intensification of adhesive interaction is taking place on the boundary between epoxy binder and glass fiber. This assumption is supported by the direct experiment – by measuring the interlayer shear strength (τ_z) Table V presents values of τ_z for VPS-7 under various doses of radiation after 2 years of exposure in a moderate climate (Zvenigorod).

TABLE V

Duration of ageing (Years)	T_0, *K*	ΔT_{∞}, *K*	T_{∞}, *K*	$k \cdot 10\, MGy^{-1}$
0	390	65	325	0.53
0.5	401	58	343	1.6
2	401	46	355	2.5
5	373	34	339	1.3

It turned out that after exposing the climatically aged VPS-7 samples to the radiation dose of 30 MGy, indicator τ_z increases by 17%.

Calculated from formula (2), values of T differ from the experimental ones tabulated in Table V by no more than 3 K.

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