

EFFECT OF PROLONGED ATMOSPHERIC AGING ON THE PROPERTIES AND STRUCTURE
OF CARBON PLASTIC*

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Modern polymeric composite materials (PCM) exhibit relatively elevated climatic stability [1], but in prolonged exposure to climatic factors, their properties can change. The extensive use of these materials in different branches of modern technology poses the problem of a complex study of the mechanisms of atmospheric aging of PCM.

Studies of the changes in the mechanical properties, thermal expansion, thermal stability, and microstructure of a unidirectional carbon plastic after 11 years of aging in the climatic conditions of the warm, humid region of Batumi [2] are reported in the present article.

A unidirectional carbon plastic based on epoxy-triphenyl (ETP) binder was selected as the object of investigation [3]. A twist of VEN-210 carbon fiber (volume degree of filling of $57 \pm 1\%$) was the reinforcing filler [1]. Sheets of the carbon plastic 2.0-2.2 mm thick were exposed on open benches according to GOST 17170-71. The samples were cut from the sheets along the fibers for mechanical and dilatometric tests. The shape and size of the samples for determining the tensile strength and modulus of elasticity on bending (subsequently indicated by σ and E) were selected according to GOST 25604-82. The characteristics of σ and E were found at temperatures of 293 and 473°K with the method in [4]. The relative elongation $\Delta l/l$ of the plastic was measured on a quartz linear dilatometer with an optical reading system in the 77-500°K temperature range with a precision of less than 1 μm . The density of the samples ρ was determined by hydrostatic weighing. The molecular mobility and relaxation processes were studied by the method of low-frequency dynamic mechanical spectrometry similar to [2, 5] to determine the molecular mechanism of the physicochemical processes which take place in the ETP binder. The temperature dependences of the dynamic shear modulus G' , the mechanical loss tangent $\tan \delta$, and the velocity of sound c_t , measured with a reverse torsion pendulum in the 77-573°K temperature range with an error of 2-4%, were analyzed for this purpose. The thermal properties of the carbon plastic were studied on a thermal analyzer in inert and oxidative media with a heating rate of 10°K/min. Scanning electron microscopy in the secondary electron mode was used to determine the structural changes in the material. The external surfaces of the samples and the surfaces of chips of the samples previously underwent ionic etching for 15 min and then ionic sputtering with gold. The samples of the carbon plastic prepared in this way were studied in a JEOL ISM-35C electron microscope.

Mechanical Properties. The kinetics of the change in the elastic-strength properties in bending of the carbon plastic after aging for up to 11 years are reported in Table 1. The value of σ measured at 293°K after 11 years of aging decreased by a total of 10%, while E decreased by 38% at this temperature. A much greater decrease in parameters σ and E (by 31 and 71%) was observed at the temperature of 473°K. The decrease in the values of the mechanical properties as a function of the aging time, as the analysis showed, was exponential. For example, the modulus of elasticity measured at 473°K obeyed the equation

$$E - E_{\infty} = (E_0 - E_{\infty}) e^{-kt},$$

where E_0 , E_{∞} are the values of the modulus of elasticity of the samples in the starting state and when $\tau \rightarrow \infty$; k is a constant. For the given case, $E_{\infty} = 48$ GPa, and $k = 0.426 \text{ yr}^{-1}$.

The temperature dependences of G' and $\tan \delta$ of the carbon plastic in the initial state and of samples after aging for 11 years are shown in Fig. 1. Figure 1 shows that the basic mechanisms of the viscoelastic behavior previously examined for PCM [2, 5] are also manifested

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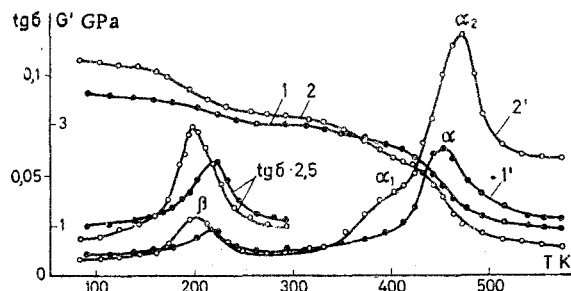


Fig. 1. Temperature dependences of G' (1, 2) and $\tan \delta$ (1', 2') of the carbon plastic in the initial state (1, 1') and after 11 years of atmospheric aging (2, 2').

TABLE 1. Mechanical Properties of the Carbon Plastic after Atmospheric Aging in the Warm Humid Zone of Batumi

Duration of aging, years	σ , GPa		E , GPa	
	at the testing temperature, °K			
	293	473	293	473
0 starting	0,80	0,45	165	145,0
1	0,75	0,39	145	120,0
3	0,71	0,37	138	76,0
5	0,75	0,35	133	—
7	0,74	0,32	122	52,5
11	0,72	0,31	102	50,0

Note. The average values of the properties are reported. Five samples were tested for each point; the coefficient of variation did not exceed 5%.

in the carbon plastic based on ETP binder. In particular, the temperature dependence of the G' of the initial samples is characterized by two segments of a decrease in G' corresponding to the pronounced mechanical loss relaxation maxima on the curve of $\tan \delta = f(T)$. The molecular mechanism of these maxima is known [2, 5]. The low-temperature β -peak of $\tan \delta$ observed at 218°K is characteristic of mobility of the local type in the macromolecules of epoxy compounds. The high-temperature α -maximum at 453°K corresponds to devitrification of the binder.

A feature of the α -peak of $\tan \delta$ in epoxy compounds is the fact that it is the superposition of two α_1 - and α_2 -maxima of $\tan \delta$ which are close together on the temperature scale [2, 5]. According to the current concepts of the structure of cross-linked polymers [6], the α_1 -maximum reflects the process of thawing of segmental mobility of the microbrownian type in an unordered polymer matrix, while the α_2 -maximum corresponds to the analogous process in structural formations with a higher density or molecular ordering. Despite the fact that the α -maximum is not distinctly divided into two separate mechanical loss peaks in the starting samples of this carbon plastic, the multiplet character of devitrification indicates the existence of four temperature transitions in the graph of $c_t = f(T)$ (Fig. 2). According to the data in [2, 5], temperatures T_1 and T_3 determine the lower and upper limits of the α_1 -relaxation process, while T_2 and T_4 indicate the beginning and end of α_2 -relaxation. It is possible to obtain important information on the resulting effect of prolonged exposure to aggressive climatic factors on the properties and structure of carbon plastics by comparing the temperature dependences of G' , $\tan \delta$, and c_t for the initial and aged samples (see Figs. 1 and 2).

After 11 years of atmospheric aging, a significant increase in the multiplet character of the α -relaxation process takes place in the ETP binder due to a shift in temperature T_1 from 401 to 328°K (see Fig. 2). The height of the high-temperature maximum of $\tan \delta$ increases by almost two times, and the α_1 - and α_2 -peaks become relatively well separated. A decrease when $T > T_4$ (in the region of the highly elastic state of the binder) and an unexpected increase when $T < T_1$ (in the glassy state) are observed in the dynamic shear modulus. The temperatures of transitions T_2 , T_3 , and T_4 increase by 10–16°K. The β -relaxation maximum is shifted by 20° to the lower temperatures and the height increases by almost 40% in the aged sample.

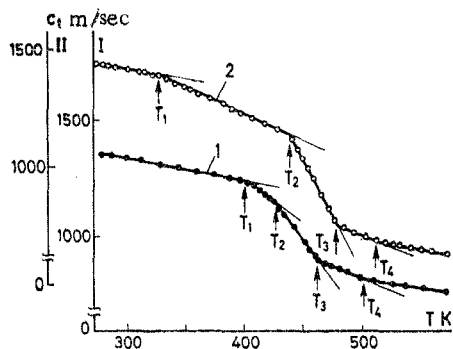


Fig. 2

Fig. 2. Temperature dependences of c_t of the carbon plastic in the region of devitrification of the binder in the initial state (1) and after 11 years of atmospheric aging (2).

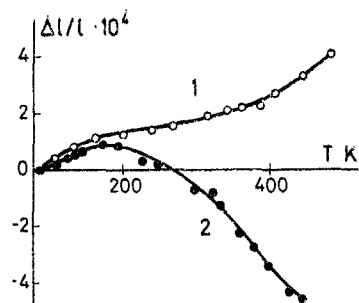


Fig. 3

Fig. 3. Temperature dependences of $\Delta l/l$ of the carbon plastic in the initial state (1) and after 11 years of atmospheric aging (2).

The intensification of the multiplet character caused by broadening of the transition zone $\Delta T_{1,3} = T_3 - T_1$ from $62^\circ K$ in the initial state to $151^\circ K$ in the samples aged for 11 years and the shift in the α_1 -maximum of $\tan \delta$ to the lower temperature region indicate structural transformations of the unordered matrix of the ETP binder. It can be concluded that an increase takes place in the bulk of the less ordered or looser sections of the matrix, i.e., an increase in the structural heterogeneity, due to processes of decomposition in the unordered regions. This effect was previously observed in an organotextolite binder [5]. The destructive processes caused marked disintegration of the ETP binder, confirmed by the decrease in the density of the carbon plastic from 1.58 g/cm^3 in the initial samples to 1.50 g/cm^3 in the samples aged for 11 years. For this reason, the conditions are facilitated for the appearance of low-temperature mobility of the local type: the number of relaxing elements increases (increase in the height of the β -maximum of $\tan \delta$) and the efficiency of the intermolecular interaction decreases (shift in the β -maximum to low temperatures).

The shift in the T_2 and T_4 transitions and the α_2 -maximum of $\tan \delta$ to higher temperatures (see Figs. 1 and 2) is similar to the previously found effects in carbon plastics based on an epoxy-aniline-phenol-formaldehyde binder [2]. Prolonged exposure to climatic factors (up to 2800 mm of precipitation a year with variations in the humidity from 30 to 100% and the temperature in consideration of radiation heating from 263 to $340\text{--}350^\circ K$, relatively high intensity of ultraviolet radiation) not only causes decomposition of the binder but also causes it to attain a deeper degree of curing. This apparently takes place both due to residues of the curing agent and due to activation of the groups formed on breaking of the stressed segments of the macrochains. The increase in temperatures T_2 and T_4 and the almost unchanged width of the transition region $\Delta T_{2,4} = T_4 - T_2$ ($74\text{--}78^\circ K$) indicate the elevated stability of the structure of the binder in the more ordered regions.

The increase in the height of the α_2 -peak of $\tan \delta$, accompanied by a decrease in G' when $T > T_4$, can be attributed to weakening of the adhesive interaction at the ETP matrix-carbon fiber interface. The overstrained bonds are apparently destroyed first, causing relaxation of internal stresses, the transition to a more equilibrium structural state, and an increase in G' when $T < T_1$.

Thermal Expansion. The temperature dependences of the change in the linear dimensions of the samples $\Delta l/l$ (Fig. 3) characterize the difference in the properties of the plastic in the initial state and after 11 years of atmospheric aging. In the initial state, the length of the sample monotonically increases with the temperature. In the aged samples, elongation is only observed up to $173^\circ K$, and shrinkage then occurs.

The qualitative difference in the course of the curves of $\Delta l/l = f(T)$ shown in Fig. 3 confirms the conclusion on the difference in the adhesive interaction of the ETP binder with the filler before and after aging. Due to the linear thermal expansion coefficients of different signs (positive in the binder and negative in the carbon fiber [7]), two mutually

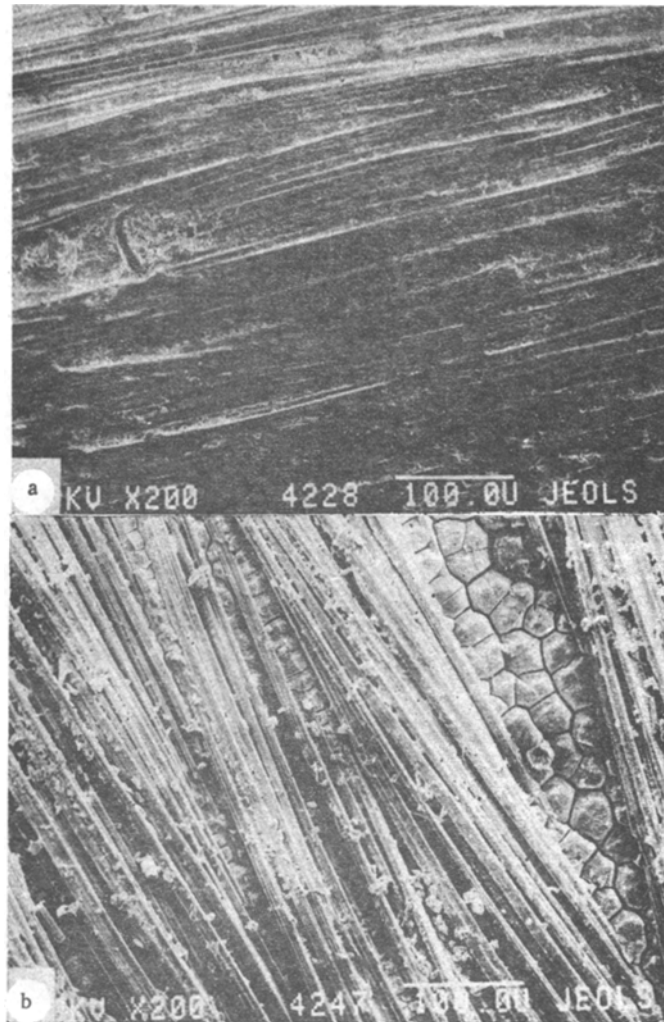


Fig. 4. Structure of the surface of the plastic in the initial state (a) and after 11 years of atmospheric aging (b). Magnification 200 \times .

competitive processes take place with an increase in the temperature: expansion and shrinkage. In the presence of a strong carbon fiber-binder adhesive bond [8] and different linear thermal expansion coefficients (higher in the polymer [1, 7]), elongation of the initial samples takes place with an increase in the temperature. Destruction of the adhesive bonds worsens the interaction of the filler with the binder and causes a shrinkage effect for the aged samples cut along the direction of the reinforcement.

Linear dilatometry thus confirms the effect of weakening of the adhesive interaction between the filler and binder and is the cause of the increase in the deformability of the aged samples of the plastic (see Table 1).

Microstructure. Selected results of the electron microscopic studies are shown in Figs. 4 and 5. A continuous resinous film is visible on the surface of the initial samples of the plastic (cf. Fig. 4a); it is almost totally destroyed in the aged samples, baring the fibers (cf. Fig. 4b). The resin undergoes pronounced cracking. The character of the position of the microcracks is well illustrated in Fig. 4b.

The analysis of the photomicrographs of the chips made it possible to confirm and characterize the structural changes in the bulk of the matrix and at the polymer-fiber interface (see Fig. 5). Although the matrix is in close contact with the fiber at the interface and has a comparatively homogeneous fine globular structure before aging (see Fig. 5a), after prolonged aging (Fig. 5b), the microheterogeneity of the matrix increases significantly (round regions up to 5 μm in diameter are formed), while peeling of individual sections of the matrix from the fiber is observed at the interface and peeling occurs along the boundary layer.

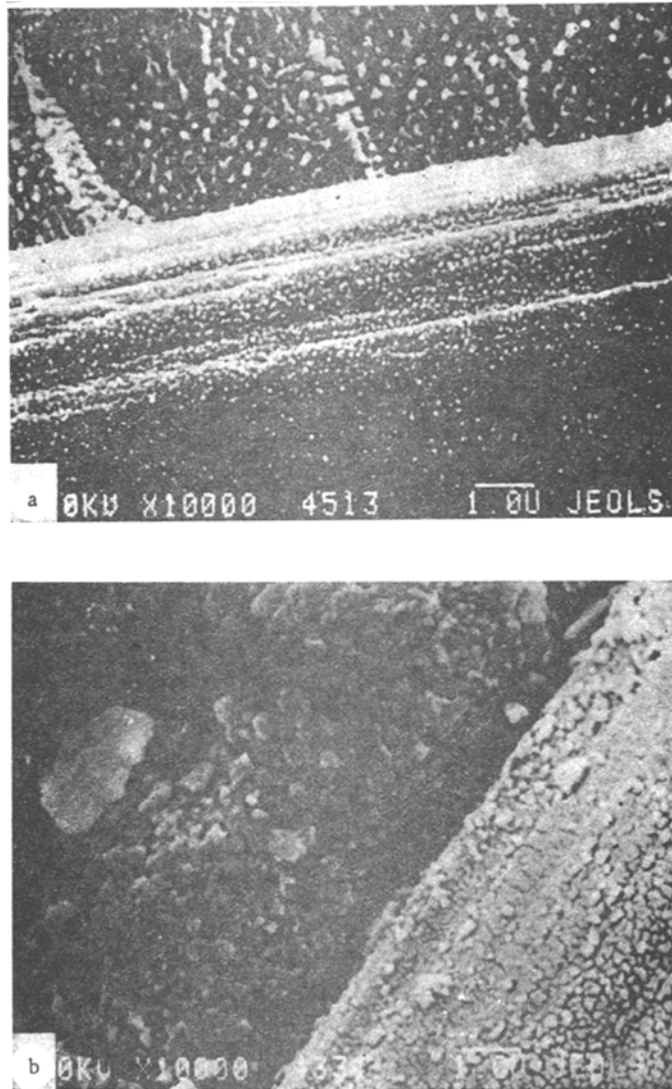


Fig. 5. Microstructure of a chip of matrix between fibers in the plastic in the initial state (a) and after 11 years of atmospheric aging (b). Magnification 10,000 \times .

An increase in the interglobular distance is observed in both the binder near the surface of the fiber and in the chip of resin far from the binder.

The observed microstructural changes in the carbon plastic during aging are in complete agreement with the conclusions formulated in the analysis of the dynamic mechanical and dilatometric results.

Thermal Properties. The results of the thermal measurements are reported in Table 2. The following changes should be noted. An increase in weight losses both in inert and in oxidizing media is observed in the temperature range preceding the basic decomposition of the binder in the carbon plastic, and this indicates an increase in the less thermally stable fraction of the polymer. If the degree of filling of the plastic is considered unchanged, the decrease in the temperatures corresponding to 5 and 10% weight losses also indicates weakening (rupture) of the chemical bonds in the polymer. The rate of maximum decomposition of the binder decreases with an increase in the aging time, which could be due to slight thermal stabilization of the polymer unit (due to attaining a deeper degree of curing and transition of the binder to a more equilibrium structural state). This is also indicated by the increase in the yield of solid residue of the composite after 1 year and 5 years of aging. Destructive processes become predominant in the samples exposed for 11 years.

TABLE 2. Thermal and Thermal-Oxidative Stability of the Carbon Plastic after Atmospheric Aging in the Warm Humid Region of Batumi

Aging time, years	Change in weight before basic decomposition, %	Weight of residue, %	Rate of maximum decomposition, %/min	Temperature, °K			heat effects
				5% weight loss	10% weight loss	max. rate of decomposition	
Thermal stability of the carbon plastic							
0	0,75	68,0	2,65	638	668...673	678	623; 698; 723
1	1,25	70,0	2,10	633...638	663...668	668	623 shoulder; 699; 723
5	1,30	72,5	1,95	618...623	643...653	663	633 shoulder; 683; 713
11	1,50	67,5	2,15	623	653	673	623 shoulder; 683; 723
Thermal-oxidative stability of the carbon plastic							
0	6,00	40,0	2,40	596...631	625...651	658	605...623; 658 shoulder; 871
1	10,20	38,8	1,50	595...623	633...661	658	596 shoulder; 653...693 shoulder; 788
5	12,00	41,6	1,50	535...625	635...660	664	623 shoulder; 673; 728; 828
11	9,40	40,8	1,60	596...628	623...663	661	623 shoulder; 661; 713; 738 shoulder; 836

The number of fractions of the binder with a different reactivity is redistributed during aging as a result of the structural rearrangements examined above. As the aging time increases, the heat release characteristic of the less thermally stable fraction of the binder (623°K) decreases in intensity. The intensity of the fraction at 698°K simultaneously increases, and its position is shifted to the lower temperature region after 5 years of exposure. In an oxidizing medium, the processes are leveled and the differences in the properties are less pronounced. It can be concluded that the results of studying the thermal properties also suggest the occurrence of two competing processes: additional hardening with short exposure times and decomposition with long aging times. This does not contradict the conclusions in [2, 5].

On the whole, the results of the mechanical and thermophysical studies and the microstructural analysis are in good agreement and sufficiently convincingly reveal the molecular mechanism of prolonged atmospheric aging of a carbon plastic in a humid subtropical climate.

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