Mechanics of Composite Materials, Vol. 30, No. 2, 1994

INTERPRETATION OF THE ANOMALOUS CHANGE IN THE PROPERTIES OF CARBON-FIBER-REINFORCED PLASTIC KMU-1u DURING AGING IN DIFFERENT CLIMATIC REGIONS

Yu. M. Vapirov, V. V. Krivonos, and O. V. Startsev

It is known that the rate of change in the main service characteristics of carbon-fiber-reinforced plastics during aging depends on the specific climatic conditions. In a number of cases, conventional representations indicating an increase in the aggressiveness of the climate with an increase in relative humidity [1] have not been supported by the experimental data for the given class of materials [2].

Our goal here is to explore the reasons for the anomolous change in the properties of carbon-fiber-reinforced plastic KMU-1u after aging for 10 yr in the warm, moist climate of Batumi and the moderate climate of Zvenigorod. It turned out that characteristics of the material such as strength σ_{bn} and elastic modulus E_{bn} in bending and strength in compression σ_{-u} were higher in the former climate than in Zvenigorod (Table 1).

Specimens of KMU-1u fully coated with lacquer were exposed under the given climatic conditions on open platforms (the dark-green VÉ-14 coating remained intact during the entire period of aging, with some reduction in coating thickness having occurred on the exposed side). The following quantities were measured in both the initial specimens and the exposed specimens: dynamic shear modulus G′; loss tangent tan δ; low-frequency shear wave velocity c_t in the temperature range 93-573 K; thermal expansion $\Delta l/l_0$ in the range 293-493 K; density ρ; σ_{bn} and E_{bn} at 293 and 473 K (in accordance with GOST 25604−82) and σ_{-u} at 293 and 473 K (in accordance with GOST 25602−80). The method of free torsional vibrations [3] was used on a torsion pendulum [4] to measure dynamic characteristics G′, tan δ, and c_t. Thermal expansion was evaluated on a quartz linear dilatometer [5]. Density was determined by hydrostatic weighing.

The specimens were in the form of slabs 2 mm thick with a (0°/90°/0°) structure. The specimens were cut out along the direction of reinforcement of the outer layers (0°). Before the exposed specimens were tested, the lacquer coating was removed mechanically without damage to the specimen surface.

We also conducted a preliminary experiment which showed that, with an accuracy sufficient for engineering calculations, the dynamic shear modulus G′ measured within the frequency range 0.5-10 Hz coincides with the static shear modulus in the reinforcement plane G_{xy}. The latter was measured by the method described in [6].

The specimens exposed to the Batumi and Zvenigorod climates had moisture contents of 0.8 and 0.5% (respectively) and were not dried prior to the mechanical and thermal tests.

To explain the differences in the climatic stability of the plastic, we will examine the temperature dependences of G′, tan δ (Fig. 1), c_t (Fig. 2a) and $\Delta l/l_0$ (Fig 2b). We note the presence of the two relaxation regions characteristic of carbon-plastics in the initial specimens (curves 1, 1′ in Fig 1). The first, located within the temperature range 93-365 K, corresponds to the glassy state of the binder. The decrease seen in the shear modulus G′ within the given region as temperature increases is accompanied by the appearance of the β-peak of tan δ, with a maximum at 208 K. This maximum is attributable to the "unfreezing" of local types of molecular motion [3]. The second region, associated with the temperature range 365-493 K, appears as a result of the transition of the binder from the glassy state to the highly elastic state. This region is characterized by a sharp decrease in G′ and the appearance of the α-maximum of tan δ, which is due to the "unfreezing" of segmental mobility in the network polymer [3]. At T > 493 K, the binder is in the highly elastic state and G′ undergoes almost no

Sochi Scientific Research Center, Russian Academy of Sciences. All-Russian Scientific Research Institute of Aviation Materials, Moscow. Translated from Mekhanika Kompozitnykh Materialov, Vol. 30, No. 2, pp. 266-273, March-April, 1994. Original article submitted January 11, 1994.

 0191-5665/94/3002-0190$12.50

TABLE 1. Strain–Strength Properties of Carbon-Plastic KMU-1u After Aging for 10 Years in the Climates of Batumi and Zvenigorod*

Characteristic	Test temperature, K	Initial value of the characteristic	10 years of aging	
			Batumi	Zvenigorod
σ_{bn}, MPa	293	480	494	439
	473	300	275	206
E_{bn}, MPa	293	88	92,5	65
	473	70	50	25
σ_{-u}, MPa	293	260	256	242
	473	160	131	128

*Mean values of the characteristics are shown. At least five specimens were tested to obtain each point. The coefficient of variation did not exceed 6%.

change. The region in which the binder goes from the glassy to the highly elastic state is a multiplet region, as is indicated by the presence of four temperature changes on the temperature dependence of c_t (curve 1 in Fig. 2a) calculated from the formula $c_t = \sqrt{G'/\rho}$. According to current thinking [7], the T_1 and T_3 transitions correspond to the temperatures at which the unfreezing of segmental mobility begins and ends in the less ordered regions of a network polymer, while T_2 and T_4 correspond to the same in the more ordered structural components.

An analysis of the temperature dependences of G′, tan δ, and c_t (Figs. 1 and 2a) permits the conclusion that final curing and degradation took place in the binder of the specimens during the climatic tests. Support for this conclusion comes from the increase in the glass point T_2 and the T_3 and T_4 transitions, as well as from the shift of the α-maximum of tan δ to a higher temperature region. Evidence of the occurence of degradation includes the decrease in T_1 and the appearance of an additional α_1-maximum of tan δ on the low-temperature branch. Similar results were obtained in [8, 9] in the aging of carbon-plastics.

In comparing the efficiency of the different structural changes that take place in the binder of the given plastic after aging in different climates, we find that cross-linking occurs more rapidly in the Batumi climate than under the climatic conditions in Zvenigorod. Conversely, degradation or damage accumulation proceeds farther in specimens exposed to the Zvenigorod climate. In fact, the specimens tested in the moister climate were cured to a greater extent, to judge from the high value of G′ at $T > T_4$, the decrease in the height of the maximum of tan δ, the higher values of T_3 and T_4, and the higher α-maximum of tan δ under the given conditions (Figs. 1 and 2a). At the same time, the lower value of T_1 and the shear modulus G′ in the glassy binder and the higher values of α_1- and β-maxima of tan δ in the specimens exposed to the moderate climate show that degradation occurs more intensively under such conditions. Here, it is important to determine which of the above processes will dominate during a given stage of aging in specimens exposed to different climates.

We should first of all note the increase in the volume of the less ordered structural components of the specimens in all of the tests due to degradation. This can be seen from the broadening of the transitional region $\Delta T_{13} = T_3 - T_1$ from 98 K in the initial specimens to 128 and 142 K after aging for 10 yr in the moist and moderate climates. A further indication of an increase in the volume of the less ordered structures is the value of the α_1-maxima of tan δ.

Being the reason for the increase in free volume in the binder, degradation processes can also be cited as the reason for the denser packing of the polymer in the glassy state as temperature decreases. Such a change should be reflected in the value of the defect modulus $\Delta G'/G' = (G'_1 - G'_2)/G_2$ (where G'_1 is the shear modulus measured at T = 98 K and G'_2 is the same measured at T = 400 K). In fact, whereas this quantity had a value of 0.5 in the initial specimens, its value increased to 0.7 and 1.6 in the specimens tested in the moist and moderate climates, respectively. Since the values of $\Delta G'/G'$ for the aged specimens turned out to be higher than the values for the initial specimens, it can be concluded that degradation was the dominant process in the specimens exposed to climate for 10 yr. This conclusion is backed up by the dilatometric characteristics shown in Fig. 2b. It is apparent from the figure that the greatest shrinkage is seen in the initial carbon-plastic specimens within the temperature range 293-493 K, due to the negative coefficient of linear expansion of the carbon fibers

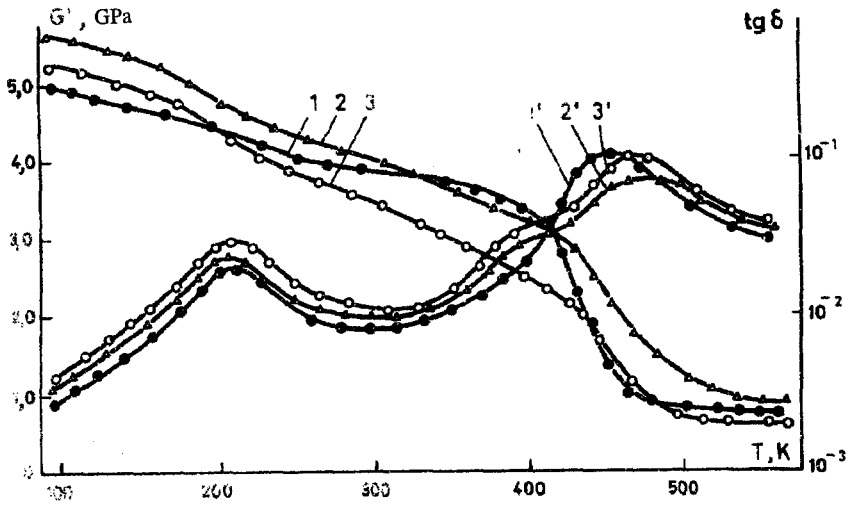

Fig. 1. Temperature dependences of G′ (1-3) and tan δ (1′-3′) for carbon-plastic KMU-1u in the initial state (1, 1′) and after aging for 10 yr in the climates of Batumi (2, 2′) and Zvenigorod (3, 3′).

[10]. Shrinkage was less pronounced in the aged specimens, which can be attributed to a weakening of intermolecular interaction due to the decrease in the density of the binder. These results also provide evidence that degradation took place more intensively in the specimens exposed to the moderate climate.

It is interesting that none of the specimens showed signs of a deterioration in adhesive interaction at the interface between the fibers and the polymer matrix. Yet such an effect was observed in [8] in carbon-plastic KMU-1, which – as the KMU-1u we studied – has an epoxytriphenol binder but a different filler (the filler in KMU-1 consists of VÉN-210 roving, while the filler in KMU-1u is VMN-4 roving). In contrast to KMU-1, the VMN-4 filler of KMU-1u forms a transitional layer which is highly stable against climatic effects.

In order to understand the reasons for the differences in the resistance of the carbon-plastic to the climatic effects encountered in the two regions chosen for study, it is necessary to evaluate the effect of the moisture content of the specimens when the measurements were made. As is known [11] moisture has a plasticizing effect, resulting in a reduction in the elastic properties of the composite (regardless of whether the binder is in the glassy or the highly elastic state), a decrease in T_1-T_4, and an increase in the heights of the α- and β-maxima of tan δ. The measured quantities were greater, the higher the moisture content of the composite.

The effect of moisture content was greatest within the temperature range 93-373 K for the given carbon-plastic, since the amount of moisture in the specimen decreased rapidly with a further increase in temperature. Since the moisture contents of the specimens exposed to the moist and moderate climates were 0.8 and 0.5%, respectively, we should have expected to see lower values of G′ and T_1 and a higher β-maximum of tan δ in the specimens exposed to the moist climate. However, as can be seen from Fig. 1 and Fig. 2a, these results were obtained in the specimens exposed to the moderate climate – with a lower relative humidity. Thus, at the given stage of aging, the moisture in the specimens has significantly less effect on the viscoelastic properties of the carbon-plastic than do previous physicochemical processes.

Consequently, the changes which occur in the viscoelastic properties of the glass-plastic during aging are due primarily to the combined effect of cross-linking and degradation. Here, the former process proceeds more rapidly in the specimens exposed to the moist climate, while degradation occurs most intensively in the specimens tested in the moderate climate. At the same time, degradation processes turn out to be dominant over the 10-yr aging period in both climates. These results are consistent with the data shown in Table 1, from which it is evident that elastic modulus and strength in bending measured at 293 K remained almost unchanged after aging in the moist climate but decreased by 26 and 31%, respectively, after aging in the moderate climate. The total reductions in these characteristics at 473 K were 29 and 9% after aging in the Batumi climate and 64 and 31% after aging in the Zvenigorod climate. Examination of the values of compressive strength revealed a similar pattern.

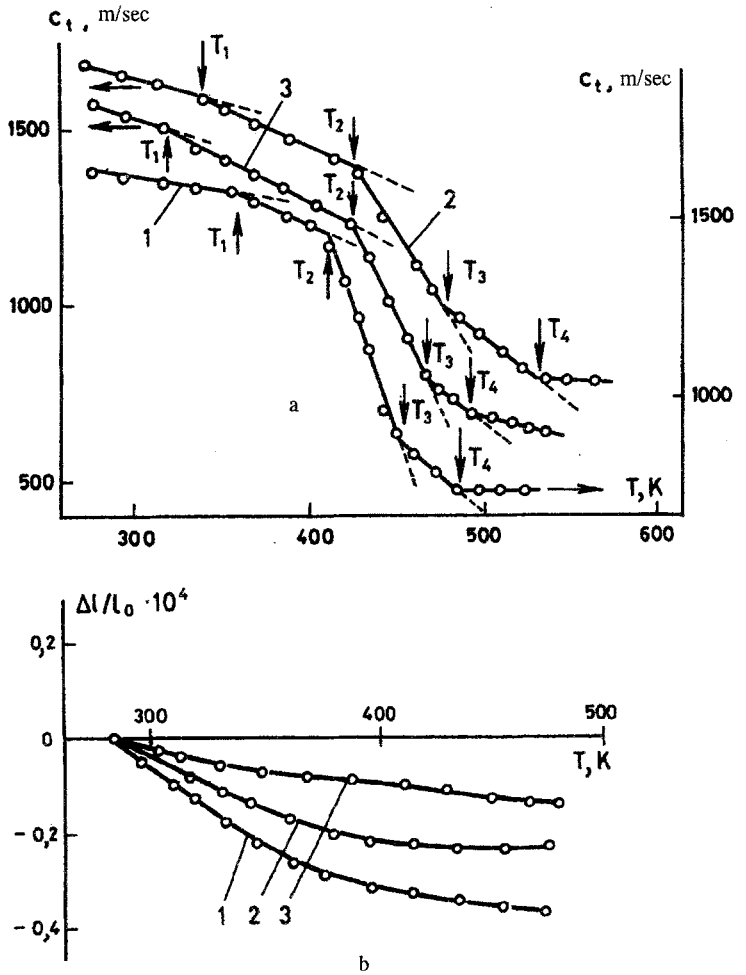

Fig. 2. Temperature dependences of c_t (a) and $\Delta l/l_0$ (b) for carbon-plastic KMU-1u in the initial state (1) and after aging for 10 yr in the climates of Batumi (2) and Zvenigorod (3).

The following can be concluded from a comparison of our data with data on the atmospheric stability of KMU-1 reported in [8]. Degradation processes occurring in the material during aging apparently have the greatest effect on the strain properties of the composite when it is subjected to bending. The size of the decrease in σ_{bn} probably depends most on the efficiency of the adhesional interaction that takes place at the polymer–filler interface.

It is also apparent from the results presented here that the more rapidly final curing of the binder proceeds, the more resistant the material will be to climatic effects, i.e. the additional cross-links that are formed will partially compensate for degradation processes that adversely affect strain-strength characteristics. Thus, the main factors that are operative in a warm moist climate have a more favorable effect in regard to final curing of the binder. Moisture is likely to be one such factor, the moisture content of specimens tested in this climate being higher than that of specimens exposed to a moderate climate.

It is now known [12] that the moisture sorbed by a polymer (in an experiment conducted on thin polymer films of the epoxide type) weakens physical bonds in the material, resulting in more rapid molecular motion. This in turn increases the probability that unreacted groups that are capable of reacting will come into contact with one another and, thus, that chemical cross-links will be formed. Under natural climatic conditions, temperature is another factor that intensifies molecular motion. According to our data, temperature reached 348 K for the given carbon-plastic as a result of radiative heating. The importance of the catalytic effect of moisture on final curing of the binder can be seen from the results of an experiment we performed on specimens of carbon-plastic KMU-3LN (with an epoxyanilinophenolformaldehyde binder). The specimens were held in water for 169 days at temperatures of 293, 323, and 353 K. Here, the specimens sorbed 0.95, 1.18, and 1.3% moisture, respectively. One of the characteristics we used to evaluate the changes in the degree of cross-linking was the glass

point T_g. It turned out that after drying until weight stabilized, the value of T_g remained at the previous level for the carbon-plastic containing 0.95% moisture, increased by 4 K for the carbon-plastic with a moisture content of 1.18%, and increased by 24 K for the carbon-plastic with a moisture content of 1.3%, i.e. the higher the moisture content of the composite and the higher the temperature, the more rapidly curing proceeds toward completion.

Thus, the additional curing that takes place in the binder of carbon-plastic KMU-1u after 10 yr of exposure to a warm moist climate due to the catalytic effect of moisture is partially offset by a decline in the strain–strength indices of the composite due to degradation. This explains the anomaly observed previously.

REFERENCES

1. I. S. Filatov, Climatic Stability of Polymers [in Russian], Nauka, Moscow (1983).
2. V. A. Yartsev, L. A. Lukashina, E. A. Mitrofanova, and N. I. Konkin, "Behavior of carbon-plastics when exposed to intense solar radiation," Summary of Documents of the Republic Interdepartmental Seminar-Conference "Processing, Degradation, and Stabilization of Polymers," Dushanbe (1983).
3. I. I. Perepechko, Acoustic Methods of Studying Polymers [in Russian], Khimiya, Moscow (1973).
4. O. V. Startsev, V. P. Meletov, and Yu. M. Vapirov, "Torsion pendulum for measuring the viscoelastic properties of materials," USSR Inventor's Certificate No. 1221542 Otkrytiya. Izobret., No. 2, 199 (1986).
5. O. V. Startsev and V. P. Rudnev, "Change in the structural nonuniformity of epoxy compounds with saturation by water," in: Aviation Materials. Corrosion and Aging of Materials in the Marine Subtropics, ONTI VIAM, Moscow (1983), pp. 71-78.
6. Yu. M. Tarnopol'skii and T. Ya. Kintsis, Statistical Testing Methods for Reinforced Plastics [in Russian], Khimiya, Moscow (1981).
7. O. V. Startsev and I. I. Perepechko, "Molecular mobility and relaxation processes in the epoxy matrix of a composite. 1. Effect of the type of reinforcing filler," Mekh. Kompozitn. Mater., No. 3, 387-391 (1984).
8. O. V. Startsev, Yu. M. Vapirov, I. S. Deev, V. A. Yartsev, V. V. Krivonos, E. A. Mitrofanova, and M. A. Chubarova, "Effect of long atmospheric aging on the properties and structure of carbon-plastics," Mekh. Kompozitn. Mater., No. 4, 637-642 (1986).
9. O. V. Startsev, G. P. Mashinskaya, and V. A. Yartsev, "Molecular mobility and relaxation processes in the epoxy matrix of a composite. 2. Effects of aging in a subtropical climate," Mekh. Kompozitn. Mater., No. 4, 593-597 (1984).
10. A. B. Geller and K. E. Perepelkin, "Features of thermal strains of carbon and organic reinforcing fibers and composites based on them," in: Composite Materials [in Russian], Nauka, Moscow (1981), pp. 228-230.
11. I. M. Barton and D. C. L. Gremfild, "The use of dynamic-mechanical methods to study the effect of absorbed water on temperature-dependent properties of an epoxy resin-carbon fibre composite," Brit. Polym. J., **18**, No. 1, 51-56 (1986).
12. Yu. S. Kochergin, G. A. Kulik, A. F. Pryadko, T. P. Slyusarenko, I. I. Dubovik, Yu. S. Zaitsev, A. A. Askadskii, and G. L. Slonimskii, "Mechanism of the effect of water on the properties of epoxy polymers," Plast. Massy, No. 11, 29-31 (1985).