MOLECULAR MOBILITY AND RELAXATION PROCESSES IN AN EPOXY MATRIX* 2. EFFECTS OF WEATHERING IN HUMID SUBTROPICAL CLIMATE†

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Previously it was shown [1] that such macroscopic visoelastic characteristics of epoxy-based polymer composite materials (PCM) as dynamic shear modulus G', loss tangent tan δ, and velocity of low-frequency shear waves $c_t = \sqrt{G'/\rho}$, where ρ is the polymer density, depend on the molecular mobility and relaxation processes in a binder. The most distinctive relaxation process is the α-relaxation caused by the transition of an epoxy matrix from the glassy to the viscoelastic state. The multiplicity of the α-transition previously observed and discussed can explain the peculiarities of viscoelastic behavior of PCM based on the concept of two levels of supermolecular organization in thermosetting polymers [2, 3].

The objective of this work was to continue the study of the molecular mobility and relaxation processes in an epoxy matrix of PCM after extended exposure to the humid subtropical Batumi climate. The combination of such factors as the high average annual relative humidity (80-85%), the large amount of precipitation (2500-2800 mm per year), the fairly high level of sun radiation, and the proximity to the Black Sea, which increases the level of sulfates and chlorides in the atmosphere, results in a highly agressive environment in Batumi. An additional factor is the natural thermocycling taking place due to radiative heating of the sample surface. For example, on sunny summer days the temperature of organic fiber-reinforced plastic samples usually reaches 320-330°K. It was thought that the degradation and cross-linking which may take place in a binder would have a considerable influence on the properties of an epoxy matrix during extended outdoor weathering. First of all, it would affect the character of the molecular mobility and relaxation processes.

In addition to the main objective of this work the elucidation of the aging mechanism in PCM has been of scientific and practical interest since the mechanism of weathering in structural plastics is not fully understood [4].

Samples of PCM based on an epoxyanilinophenol-formaldehyde binder were chosen for this investigation. A vnilivlon fiber cloth and a carbon fiber tape, LU-3, were used as reinforcing fillers in organic fiber- and carbon fiber-reinforced plastics, respectively [1]. The test samples, 250 × 250 × 1.8 mm plates, were exposed for five years. After exposure, samples were cut into 120 × 10 × 1.8 mm plates and subjected to vacuum treatment at room temperature until their mass stabilized. Then such parameters as G', tan δ, and c_t were determined at the 77-570°K temperature range with a 2-4% error by using the reverse torsion pendulum [2]. These results are presented in Figs. 1 and 2. It was shown earlier [1] that an organic fiber is the filler that most affects the structure of an epoxy binder even during hardening. Compared to organic fiber-reinforced plastics, the binder in carbon fiber-reinforced plastics has a greater density of the three-dimensional network and a greater orientation of elements of macromolecules near the filler surface. This explains the different temperature ranges of the relaxation transitions in the initial samples. Without going into the details of the molecular mobility and relaxation processes of the composites as was done earlier [1], we point out that the temperature dependences of G', tan δ, and c_t in the control samples were not noticeably changed after five years in the laboratory.

The difference in the overall effects of the agressive factors on a binder in organic fiber- and carbon fiber-reinforced composites turned out to be the most important feature of outdoor weathering.

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†For Part 1, see [1].

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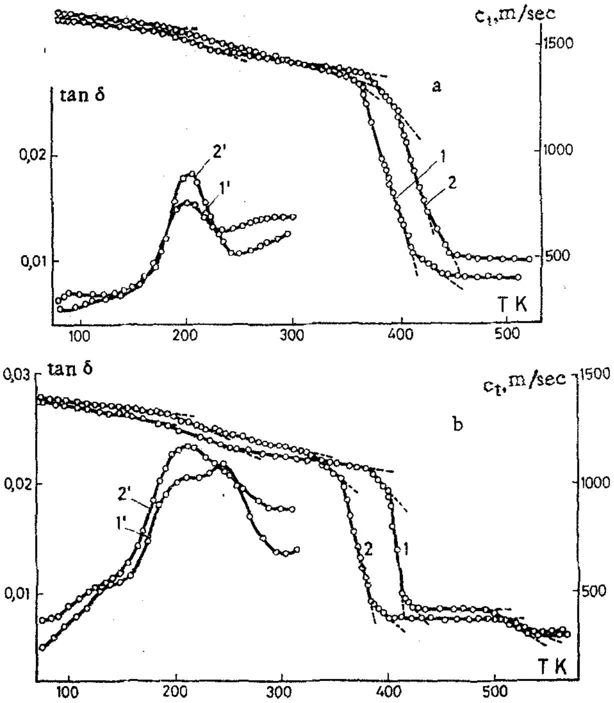

Fig. 1. Temperature dependences of c_t (1, 2) and tan δ (1', 2') in (a) carbon fiber- and (b) organic fiber-reinforced plastics in the initial state (1, 1') and after 5 years of outdoor weathering (2, 2').

Indeed, let us analyze how the temperature dependences of c_t and tan δ are changed after weathering in a carbon fiber-reinforced plastic (Figs. 1a and 2a). The α-maximum of tan δ produced by the superposition of the two peaks (α_1 and α_2) close to each other on the temperature scale [1] was shifted higher by 27°K with an increase of 25% in its magnitude. Similar shifts were found for the T_1-T_4 transition temperatures determined from the $c_t = f(T)$ curve. Temperatures T_1 and T_3, as was suggested earlier [1], determine the lower and the upper limit of unfreezing of the segmental motion in the less oriented or loosely packed regions of an amorphous thermosetting polymer. The width of the transition zone in the less oriented ($\Delta T_{13} = T_3 - T_1$) and in the more oriented ($\Delta T_{24} = T_4 - T_2$) regions of a polymer matrix was affected differently by outdoor weathering, with ΔT_{13} remaining practically unchanged (60 ± 1°K), whereas T_{24} decreased after weathering from 78 to 50°K. The increased height of the composite α-peak (curve 1' in Fig. 2a) is apparently brought about by the more cooperative character of the α_2-transition [1] as indicated by significant narrowing of the transition zone ΔT_{24}. This narrowing, as shown in Fig. 1, is the result of increasing the glass transition temperature T_2 by 33°K.

Opposite effects are produced in a binder by weathering of organic fiber-reinforced plastics (Figs. 1b and 2b). In the main relaxation region, the α-maximum tan δ decreased in magnitude and shifted to a lower temperature by 38°K. Even larger shifts were observed for the T_1-T_4 transition temperatures. The glass transition temperature T_2, for example, decreased from 405 to 360°K. Both transition zones ΔT_{13} and ΔT_{24} significantly increased: from 33 to 60°K for T_{13} and from 24 to 45°K for T_{24}, indicating the less cooperative character of the α_1- and α_2-transitions.

Thus, the obtained data led to the rather unexpected conclusion that the weathering mechanism of an epoxy matrix is different in carbon fiber- and organic fiber-reinforced plastics.

Let us consider a probable molecular mechanism of the changes taking place in the polymer matrix of composites during weathering. The changes observed in the $c_t = f(T)$ and tan $\delta = f(T)$ graphs of a carbon fiber-reinforced plastic suggest that extended outdoor weathering is favorable for achieving a higher degree of hardening of a binder. This is apparently caused by some hardener still remaining in the system as well as by active groups formed by cleavage of the most stressed segments of macrochains. The fact that the sound velocity of a binder in the viscoelastic state increased by almost 20% after weathering also suggests a higher degree of hardening after outdoor weathering because it was shown [2] that in thermosetting polymers an increase of c_t at $T > T_4$ correlates with an increase in the degree of cross-linking ν_c.

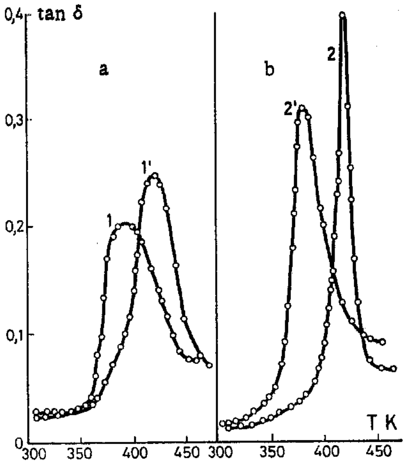

Fig. 2. Temperature dependence of tan δ in the main relaxation region of a binder in (a) carbon fiber- and (b) organic fiber-reinforced plastics in the initial state (1, 2) and after 5 years of outdoor weathering (1', 2').

Along with the increase of ν_c in a carbon fiber-reinforced plastic, the degree of structural order in the most densely packed regions of a binder also increases. This is indicated by several factors already mentioned, namely the increase in magnitude of the α-maximum, the narrowing of the ΔT_{24} transition zone, and the increase in composite density from 1470 to 1490 kg/m^3 after weathering. We can also point out that there were no visible signs of degradation in the carbon fiber-reinforced plastic.

However, in an organic fiber-reinforced plastic the possible hardening of the binder due to weathering was masked by clearly visible degradation. This degradation is indicated by the shift to lower temperatures of the α-maximum and the T_1-T_4 transitions, by the decrease in the α-peak amplitude, and by the increase of the transition zones ΔT_{13} and ΔT_{24}. The decrease of the sound velocity c_t of a binder in the viscoelastic region and, therefore, the decreased cross-linking density ν_c, also indicates that outdoor weathering results in a less densely packed network. The shift of the T_1 transition to a lower temperature region (see Fig. 1b) is only slightly larger than the corresponding shift of T_2 (56 and 45°K, respectively) and, therefore, it can be concluded that degradation involves not only the unoriented or less densely packed regions of a binder, but also the more oriented and more densely packed regions.

Now we focus on changes in the character of the molecular mobility in an epoxy matrix of PCM in the glassy state. The "anomalous" dependence of the dynamic shear modulus and the sound velocity on the degree of cross-linking ν_c is typical for epoxy compounds [2]. This is exhibited by a decrease of G' in the glassy state though the network density increases. This observation is also valid (see Fig. 1) for PCM based on an epoxyanilinophenol-formaldehyde binder. In both organic fiber- and carbon fiber-reinforced plastics, an increase of ν_c results in a decrease of the sound velocity c_t in the glassy state (at $T < T_1$). Thus, in carbon fiber-reinforced plastics increased cross-linking of the binder during outdoor weathering makes it more difficult for kinetic elements of neighboring chains to approach each other at lower temperatures, limiting, therefore, the efficiency of intermolecular interactions. As a result, in the glassy state a binder with a higher degree of cross-linking has greater molecular mobility. Such an effect caused by outdoor weathering of a carbon fiber-reinforced plastic is observed in the low-temperature region. As can be seen in Fig. 1a (curves 1' and 2') the intensity of the β-maximum, caused by unfreezing of the local molecular elements [2], increases after weathering.

It might appear that after weathering, the intensity of low-temperature mobility in a binder of an organic fiber-reinforced plastic should be reduced because of the decreased density of the three-dimensional network. Therefore, this plastic would be expected to have a reduced low-temperature β-maximum, which is a superposition of β-relaxation processes in the binder (200–210°K) and in the organic fiber (250°K) [1]. However, an increase of the β-maximum (Fig. 1b, curves 1' and 2') was observed. Apparently the intensity of the molecular mobility at low temperatures increases due to the increased amount of small kinetic elements formed during degradation of the binder. The density of an organic fiber-reinforced plastic after weathering remains practically unchanged (1250 and 1256 kg/m^3).

The results discussed here cannot yet explain unambiguously the differences in the mechanism of weathering of organic fiber- and carbon fiber-reinforced plastics. Among possible contributing factors are differences in the initial structural order, which depends on the reinforcing filler [1], or the fairly high hydrophilicity of an organic fiber [5], which increases the rate constant of degradation of an organic fiber-reinforced plastic. It is important to point out that in predicting the behavior of composites with different reinforcing fibers in an aggressive environment, one should not assume identical changes in the structure and properties of the epoxy matrix in these PCM during aging.

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ROTATIONAL DEFORMATION IN DISPERSE-STRENGTHENED COMPOSITE MATERIALS*

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Experimental investigations of recent years have established that the mechanical behavior of various solids is determined in many cases by deformation processes of the rotational type, which are associated with the mutual turning of volumes of material. For an adequate theoretical description of rotational modes of plastic deformation, it is necessary to draw upon disclination notions [1]. Among other things, the highly prevalent phenomenon of twin and kink-band formation, the development of which, from the macroscopic standpoint, is equivalent to the dipole motion of partial wedge-shape disclinations [2, 3] can be applied to rotational deformation. The latter case makes it possible to examine twinning and kink formation as elementary processes of rotational deformation.

In composites, rotational modes play a special role, since they may manifest themselves here, in contrast to homogeneous crystals, even with small degrees of deformation; this is dictated by the initial inhomogeneity of the plastic properties of composite materials [4]. Mechanical twinning without prior deformation via slipping was actually observed during the tensioning of disperse-strengthened Cu–Al–Co alloys [5, 6]. Twins have also been detected in the deformation bending of zinc crystals, which contain virtually nondeformable particles [7]. Kinking, in turn, is one of the basic strain mechanisms of uniaxially aligned fiber composites [8-10].

Thus, composite materials are an important subject for application of the disclination theory of rotational plasticity. We had previously performed quantitative computations of deformation and strength properties during kink formation for fibrous composites [3, 4]. The present study is devoted to theoretical analysis of laws governing the development of the rotational mode of deformation (in the form of twins and kink bands) in composites of another type, and, namely, in disperse-strengthened materials consisting of a plastic matrix and nondeformable particles. The study examines the stress that deforms the composites, and establishes the force dependence of the disperse strengthening due to the orientation and shape of the inclusions, as well as predicts the extrusion effect of particles from the kink bands and twins.

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