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QUANTITATIVE ASSESSMENT OF THE KINETICS OF DAMAGE ACCUMULATION IN THE POLYMER MATRIX STRUCTURE UNDER FULL-SCALE CLIMATIC FACTORS AND TENSILE LOADS *

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Statement of the problem. In the current study we look at the change in the elastic-strength performance and kinetics of damage accumulation in epoxy polymers under tensile loads in the control state and after full-scale climatic exposure during one calendar year were studied. Damage accumulation kinetics was calculated based on the author's method using methods of fractal analysis of deformation curves for polymer materials samples under tension.

Results. We proposed specific index θ to quantify the total number of damages per unit of strength, where its accumulation leads to the destruction of polymers. We obtained approximating dependences that describe the relationship between specific index θ and tensile strength of epoxy polymers.

Conclusion. The study has shown that the Etal-247 epoxy resin-based polymer cured with Etal-1440 amine hardener has the most stable properties under the full-scale climatic exposure.

Keywords: epoxy polymers, deformation curves, tensile strength, tensile elongation, damage accumulation, fractal analysis, specific index of damage accumulation.

Introduction. Polymers and polymer-based composite materials are widely used in lots of industries: electronics, mechanical engineering, construction, production of pipes, vessels, etc. [3, 5, 9, 10, 20].

The global market of polymer composite materials (PCM) has been continuously growing over the past few years. According to various estimates, it amounted to about \$90.6—93.6 billion and 120 million tons in 2019. Taking into account the forecasted aggregate average annual growth rate of about 4.0—7.7 %, by 2024 the global PCM market is set to make \$103—132 billion and 13—14 million tons [1, 2, 23, 24, 25, 31].

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In the construction industry, polymers and polymer-based composites are most commonly applied as paint and varnish materials, primers, impregnating and filling compounds, glues, etc. [7, 21]. Polymeric compositions are widely employed as decorative and protective surfacings to increase the load-bearing capacity and durability of construction materials and structures operated under aggressive climatic factors [13]. Polymer surfacings can be used to protect reinforced concrete structures and isolate the concrete and reinforcement from the aggressive environment as well as to increase the crack resistance and load-bearing capacity. The most common protective and decorative surfacings for building products and structures are compounds based on epoxy binders. This is due to a combination of high-strength and adhesive characteristics of the resulting polymeric materials [11, 13, 18, 21].

The experience of using protective and decorative coatings influenced by natural climatic factors shows [4, 6, 8, 11, 12, 14, 19, 26] that polymers age under cyclic impact of both environmental factors and mechanical loads. At the same time, the observed variation of physical and mechanical properties is associated with both irreversible changes in the properties caused by degraded surface layers of the products, polymer matrix photodestruction and chemical transformations, and reversible changes caused by sorption and desorption of environmental moisture [15, 16, 22, 30]. It is thus important to assess the contribution of reversible and irreversible components to the resulting value of changes in the polymeric material properties during full-scale climatic aging is an important task.

1. Materials and research methods. As the objects of the study, we used samples of three compounds based on ED-20, Etal-247 and Etal-370 epoxy resins and Etal-1440 amine hardener (from ENPC EPITAL JSC). ED-20 epoxy resin is a liquid reactive oligomeric product based on diglycidyl ether of biphenylolpropane. It is in compliance with the GOST R 56211-2014. The mass fraction of epoxy groups is $20 \div 22.5$ %; dynamic viscosity at 20°C is $12 \div 25$ Pa·s. Etal-247 (TU 2257-247-18826195-07) and Etal-370 (TU 2257-370-18826195-99) epoxy resins are low-viscosity modified resins with a viscosity $20 \div 22$ and $4.5 \div 5.0$ times lower than that of ED-20 epoxy resin, correspondingly. The mass epoxy group fraction for Etal-247 and Etal-370 exceeds $21.4 \div 22.8$ and 21.5 %, correspondingly.

We tested the mechanical properties of the samples of the investigated compounds using an AGS-X series tensile testing machine with TRAPEZIUM X software. The test temperature was $23 \pm 2^\circ\text{C}$ and relative air humidity was 50 ± 5 %. The tensile testing machine clamps moved at 2 mm/min with the frequency of readings of 0.01 sec . At least 6 samples were tested for each compound in parallel (type 2 according to GOST 11262-2017). The samples were

exposed on the test benches of the laboratory of environmental and meteorological monitoring, construction technologies and examinations of the Ogarev National Research Mordovia State University (Saransk).

The failure accumulation kinetics was assessed based on the results of the proprietary methodology and provided in works [27, 28, 29]. Typical curves of the fractality index change depending on the tensile elongation are presented in [28].

The paper proposes the use of the specific index θ to quantify the changing kinetics of failure accumulation in the structure of polymer samples during full-scale climatic aging exposed to the tensile loads. Specific index θ is the ratio of the fraction of accumulated failure when it reaches the maximum stresses to the polymer sample ultimate strength. The quantitative values of the fraction of accumulated failures in the polymer matrix structure was identified using the author's technique. It allows us to determine the coordinates of critical points on deformation curves detected by fractal analysis methods [11, 27, 28]. The above technique is based on the least coverage method used for analysis of various time series [17].

2. Results of the research of elastic-strength characteristics and kinetics of damage accumulation in the structure of epoxy polymers under the influence of natural climatic factors and mechanical loads. We studied the change in the elastic-strength performance and kinetics of failure accumulation in epoxy polymers exposed to tensile loads in the control state and following a full-scale climatic exposure for 45, 90, 180, 270, and 360 days. The results of changes in the elastic and strength characteristics during climatic aging in absolute and relative values are shown in Fig. 1. For the control samples, we found that the highest strength and deformation was recorded for ED-20 and Etal-370 epoxy resin-based polymers. The tensile strength and relative elongation at maximum load for the ED-20 + Etal-1440 sample is 52.9 MPa and 9.8 %, and 54.7 MPa and 11.1 % for Etal-370 + Etal-1440. Epoxy polymer samples based on modified Etal-247 resin in the control state have the tensile strength of 40.8 MPa and relative elongation of 8.6 %. It is 23÷25 % and 12÷22 % lower than those of other compounds respectively.

The field test results showed that the climatic exposure within one calendar year causes a significant decrease in the elastic-strength parameters of polymers based on ED-20 and Etal-370 epoxy resins. In particular, the loss of strength and deformation characteristics of the ED-20 + Etal-1440 compound by 360 days from the control values is 34 and 49%. Whereas, that of the Etal-370 + Etal-1440 compound is 48 and 73 %, correspondingly. At the same time, the polymer based on the Etal-247 modified epoxy resin showed a significantly greater

stability of elastic-strength characteristics. The maximum decrease in tensile strength and elongation in tension was 8 % and 23 %, in 1 year of a full-scale exposure.

In [27, 28], to assess the level of accumulated failures leading to the failure of specimens under the action of tensile loads, the team of authors proposed the use of an indicator defined as the ratio of the number of points with a fractality index of less than 0.5 to the total number of points of the deformation curve (until the level of maximum stresses is reached). The calculation of the fractality indices depending on the generated stress and relative deformation makes it possible to estimate the failure accumulation kinetics when a tensile load is applied to the sample:

$$\omega(\sigma, \varepsilon) = \frac{m_{\mu(\sigma, \varepsilon)}}{n_{\mu(\sigma, \varepsilon)}} \cdot 100 \%, \quad (1)$$

where $\mu(\sigma, \varepsilon)$ is the number of points of the studied series for which the condition $\mu(\sigma, \varepsilon) < 0.5$ is satisfied; $n_{\mu(\sigma, \varepsilon)}$ is the total number of the analyzed points.

Fig. 1. Tensile strength (a) and relative tensile elongation variations when elongating (b) epoxy polymers cured with Etal-1440, during full-scale climatic aging

Table 1 shows the values of accumulated failure corresponding to the achievement of maximum tensile loads by epoxy resins identified for different periods of a full-scale exposure. We found that the ultimate levels of accumulated failure in epoxy polymers cured with Etal-1440 under the tensile loads vary depending on the climatic aging duration from 5.27 to 6.52 %.

Failure accumulation curves for the epoxy polymers of the three investigated compounds in the control state as well as after climatic exposure for various durations are shown in Fig. 2. According to the results of the studies, significant differences in the kinetics of failure accumulation under the action of a full-scale exposure were established for polymers produced based on the ED-20 and Etal-370 epoxy resins (Fig. 2, a, b, e, f). Specifically, if for samples

of ED-20 + Etal-1440 compound at the age of 0÷90 days the share of accumulated failures at tensile load equal to 20 MPa is in the range of 25÷35 % of the limiting value, for the samples at the age of 270÷360 days it is 50÷70 % (Fig. 2, a). Failure accumulation curves for polymer based on the epoxy resin Etal-370 with an increase in a full-scale exposure duration up to 270 days smoothly shift towards lower stresses with a sharp increase for 360 days (Fig. 2, f). Analysis of changes in the accumulated failure rate depending on the level of relative elongation under tension testifies to intensification of the embrittlement process of polymers produced based on the ED-20 and Etal-247 epoxy resins in the process of a full-scale exposure (Fig. 2, b, f). Growth of failure accumulation in the polymer matrix structure with increasing duration of climatic exposure is connected with manifestation of complex influence of various factors. Hydrolysis, plasticizing effect of moisture, destruction of surface layers under the UV and solar radiation, relaxation of initial structural heterogeneity, photodestruction is accompanied by both reversible and irreversible changes in the macromolecular structure of the investigated polymeric materials.

Table 1

Numerical values of the accumulated damage frequency (%) corresponding to the achievement of maximum tensile loads by epoxy polymers, for various terms of a full-scale exposure

Epoxy resin	Full-scale exposure duration, days					
	0	45	90	180	270	360
ED-20	5.69	5.69	6.09	6.16	5.95	6.52
Etal-247	5.47	5.88	5.27	5.57	5.53	6.00
Etal-370	5.85	6.02	5.63	5.85	5.89	5.40

Analysis of the failure accumulation kinetics in the structure of the epoxy polymer Etal-247 + Etal-1440 under the action of full-scale climatic factors confirms the conclusions made earlier on the high stability of its physical and mechanical properties (Fig. 2, c, d) compared to the polymers based on ED-20 and Etal-370 epoxy resins. The failure accumulation curves as a function of the relative elongation under tension are linear for samples of all series of this compound. The maximum increase of failure accumulation rate for all time intervals of full-scale exposure of the Etal-247+Etal-1440 compound does not exceed 34÷43 %, which is 2.6÷2.7 and 2.9÷3.4 times lower than that for polymers based on ED-20 and Etal-370 respectively. Despite the lower elastic-strength parameters of the control samples of the given compound compared to the polymers based on ED-20 and Etal-370 resins, the reduction of the relative elongation characterizing the embrittlement of polymers, after 360 days of a full-scale exposure does not exceed 16 %. The variation of the critical level of tensile stresses depending on the duration of a full-scale exposure for the Etal-247 + Etal-1440 polymer does not exceed 11 %.

In order to take into account the effect of changes in the strength indices of polymers on the value of accumulated failures (until the sample reaches maximum tensile stresses), let us introduce a specific index, defined as

$$\theta = \frac{\omega}{R_s}, \quad (2)$$

where ω is the relative number of accumulated failures determined according to (1) when the sample reaches the level of maximum tensile stresses, %; R_s is the tensile strength of polymeric material, MPa.

Fig. 2. Failure accumulation curves for a series of samples of epoxy resin-based compounds: ED-20 (a), Etal-247 (b) and Etal-370 (c) cured by Etal-1440, depending on the applied stresses (a, c, e) and relative tensile elongations (b, d, f)

Fig. 3. Correlation dependences between the specific index of the number of failures θ and elastic-strength parameters (a, c, f – tensile strength; b, d, f – relative elongation) of epoxy resin-based polymers: ED-20 (a, b), Etal-247 (c, d) and Etal-370 (e, f), cured with Etal-1440

Numerical values of index θ , measured in %/MPa, for a series of samples of epoxy polymer compounds under study are shown in Fig. 3. Index θ is the specific number of failures per unit of strength. It varies for the studied compounds from 0.08 to 0.35 %/MPa. The largest scatter in the specific index θ of the studied series of samples, considering full-scale exposure duration, is observed for polymers based on ED-20 (Fig. 3, a, b) and Etal-370 epoxy resins (Fig. 3, e, f). An increased full-scale aging duration for samples of these compounds generally leads to an increased specific index θ .

Correlation dependences between specific index θ and the elastic-strength parameters of the three investigated compounds of epoxy polymers with a sufficiently high reliability (0.828 and 0.627, correspondingly) are approximated by logarithmic dependences:

$$\theta = 0.752 - 0.163 \times \ln(R_s), \quad (3)$$

$$\theta = 0.315 - 0.089 \times \ln(\Delta \varepsilon_s), \quad (4)$$

where $\Delta \varepsilon_s$ is the relative elongation of the sample when reaching the maximum tensile stresses. The possibility of approximating the values of correlation dependences shown in Fig. 3 with the general equation for all series of the studied compounds, differing in the epoxy binder type and the full-scale exposure duration, confirms the advisability of using specific index θ as a quantitative characteristic of accumulated failure, where its achievement causes the polymer destruction.

Conclusion. We found that the polymer based on the Etal-247 epoxy resin cured with the Etal-1440 amine hardener shows the highest stability of properties under the full-scale climatic exposure. Taking into account the complex of high technological indicators, this compound can be recommended as a protective and decorative surfacing of building products and structures subjected to full-scale climatic exposure.

It is suggested that the change in the failure accumulation kinetics in the structure of polymer samples is evaluated under the tensile load based on specific index θ corresponding to the number of structural elements out of serviceable state to the material strength unit. The developed approach allows one to estimate the resistance and durability of composite materials under the effect of aggressive factors, including climatic factors.

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